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THE UNIVERSITY OF ALBERTA

STUDIES OF PERCHLORATE AND CHLOROALUMINATE MELTS

by



UDO ANDERS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE  
of

DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

Fall, 1969



THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

"STUDIES OF PERCHLORATE AND CHLOROALUMINATE MELTS"

submitted by UDO ANDERS, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.



A C K N O W L E D G E M E N T S

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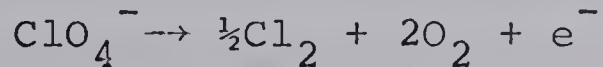


PART ITHE ELECTROCHEMISTRY OF FUSED LITHIUM PERCHLORATEA B S T R A C T

The limiting reactions which occur during electrolysis of fused lithium perchlorate are shown to be



and



at the cathode and anode respectively. The otherwise explosive reaction between the lithium metal generated and the fused perchlorate was prevented by alloying the lithium with silver. A cathodic peak observed at -1.5 volts with respect to a Ag(I)/Ag(O) electrode is attributed to the reaction



Unlike the analogous peak process observed in fused nitrates, the electron:chlorate ratio is not 2:1 even though the expected 2:1 electron:oxide ratio is obtained. This and other behavior is explained on the basis of an oxide and peroxide-catalyzed decomposition of perchlorate and chlorate.

Attempts were made to anodize metals into the melt; in no case except silver (for which the expected Nernstian behavior was observed) was this possible, oxide formation being generally observed instead.



## I N T R O D U C T I O N

The electrochemistry of molten salts has received intense study during the past decade. The increased interest in molten salts as solvents is partly caused by technical development: the application in fuel cells (1,2) is perhaps the most pertinent example at the present time. Mixtures of halides, especially the alkali halides, are generally used as solvents in technical applications due to their easy purification, high stability and wide electrochemical span.

Another important class of anions are the oxy-anions. Though not of the same technical importance as the halides they have been of considerable academic interest. The oxyanions most thoroughly investigated were the silicates (3), borates (4), carbonates (5), nitrates (6,7,8), nitrites (9,10,11), sulfates (12) and metaphosphates (13). Their most striking feature as compared to the alkali halides is the appearance of an additional cathodic peak in voltammetry in the current-voltage diagram. Consequently, one will have to discuss the reactions corresponding to the limiting reactions as well as to the cathodic peak when characterizing oxyanions. It will be shown later that the cathodic peak reaction will have a modifying effect on the cathodic limiting reaction.



The anodic limiting reactions of the oxyanions all involve oxygen evolution. The product, besides oxygen, is generally the anhydride corresponding to the aqueous acid of the oxyanion. The following examples can be stated.

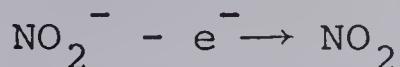
The electrolytic oxidation of carbonate was formulated (5) in the following manner:



There is, however, a deviation from 100% current efficiency in the above reaction which has been explained on the basis of a simultaneous oxidation of the platinum electrodes:



The anodic decomposition for the nitrite was first proposed by Lyalikov and Novik (10) and affirmed later by Swofford and McCormick (9) and also by Calandra and Arvia (11). The anodic process results in the production of  $\text{NO}_2$  via



The anodic overall reaction in the case of the nitrates (15) is similarly given by



Considerable controversy exists concerning the possible intermediate  $\text{NO}_2^+$  (9,15,16,17). Although the existence of the nitronium ion  $\text{NO}_2^+$  has been substantiated in



highly acidic aqueous media, it has not been observed directly in molten nitrates. Topol, Osteryoung and Christie (16) could not confirm the presence of  $\text{NO}_2^+$  with either voltammetry or chronopotentiometry. Inman and Braunstein (17), on the other hand, reported the detection of it by chronopotentiometric methods. No details, however, were given by the latter authors. No conclusion can apparently be drawn in this matter at this stage.

The anodic limiting reaction in the case of the sulfates (12) was established as



which is very similar to the metaphosphates (13) whose reaction at the anode was given by



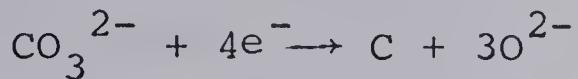
No quantitative determinations of the electron to products ratio was attempted in most of the cases.

The cathodic limiting reactions are in all cases characterized by the deposition of the cationic melt constituent. These reactions are not stoichiometric in the presence of the oxyanions. This is due to another cathodic process which will be referred to from this point on as the "cathodic peak reaction" because of the sharp peak shown in voltammetry by this reaction.



A few well-established examples for the cathodic peak reactions shall now be mentioned.

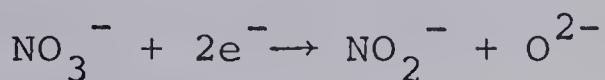
The carbonates (5) have been observed to undergo the following reaction at the cathodic peak:



CO and CO<sub>2</sub> have been discussed (5) as intermediates in this reaction.

The first discussion of the cathodic reduction of the fused nitrate anion comes from Hills and Johnson (7).

The following reaction schemes were postulated

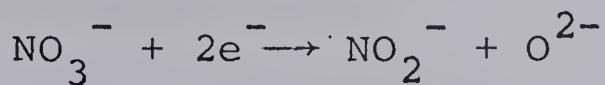


and



No quantitative analysis of the products was reported.

Swofford and Laitinen (6) reinvestigated the nitrate system and arrived at the following equation, in agreement with the equations proposed by Hills and Johnson:



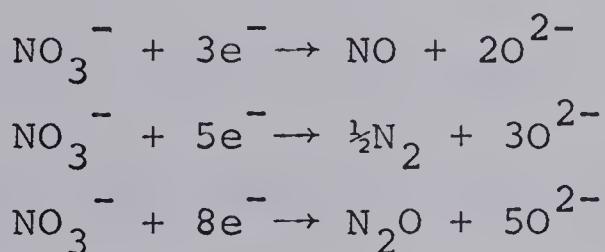
The analytical determinations of the amounts of oxide and nitrite produced by the above reaction were done as follows. The compartment analyzed for oxide was dissolved in water and the hydroxide produced titrated with standard 0.01 M HNO<sub>3</sub> while that to be analyzed for nitrite was dissolved in a standard solution of 0.01 N KMnO<sub>4</sub> and back-titrated with a solution of 0.01 N Fe(II). This



was the first procedure used to establish unambiguously the stoichiometry of a typical cathodic peak reaction.

The amounts of oxide and nitrite found (6) corresponded within a few percent to the proposed equation. The electron:nitrite:oxide ratio was close to 2:1:1.

Bartlett and Johnson (8) recently investigated the nitrate system again. They conducted preparative electrolysis at controlled potentials before, at, and after the cathodic peak. While they agreed with Swofford and Laitinen (6) that the main reaction was due to the formation of nitrite and oxide they proposed three additional side reactions:



No analytical details, however, were given for the characterization of the gaseous products.

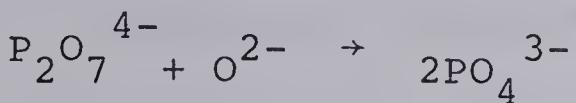
In the case of the nitrites it has so far only been shown that NO was one of the products (8) when an electrolysis was performed at the cathodic peak. Heavy corrosion of the platinum electrodes seems to have been responsible for the lack of further information.

The metaphosphates (13) undergo reaction at the cathodic peak in the following manner:





This reaction deviated from the ones before in that no oxide seemed to be formed. However, it is well known (13,18,19) that oxide reacts with  $\text{PO}_3^-$ :



and one can therefore formulate the initial reaction as



The species  $\text{PO}_2^-$ , like CO and  $\text{CO}_2$  in the case of the carbonates, is an unstable species under the experimental conditions. It is further reduced to phosphorus which is now stable:



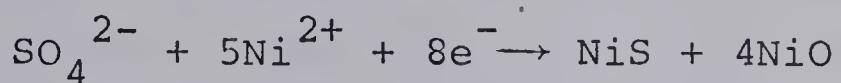
The sulfates are known to yield sulfur, sulfide, and oxide (12,14).

As can be seen it is not possible to give a general mechanism for the cathodic peak reaction. Only the primary production of oxide which may, however, as in the case of metaphosphates, undergo further reaction with the oxyanion is observed in all systems.

Since the limiting reaction occurs at a more cathodic potential than the cathodic peak reaction these two processes will occur simultaneously. This means that not only is the cation, generally an alkali metal, deposited in a pure form as in the case of the halides but at the same time oxide and other breakdown products of the



oxyanion may be co-deposited. If metal ions other than those being melt constituents have to be deposited and if their deposition potential happens to lie between the cathodic peak and the limiting reaction then there will be impurities co-deposited with the metal. A typical illustration of this fact (12) is the co-production of NiS and NiO when deposited from a solution of Ni(II) in molten sulfate:



While this process would be unwanted in the case of deposition of pure nickel the same process can be sought after in special cases. The production of a layer of GaP on pure Si (20) is such an example in which GaP was deposited from a solution of Ga(III) in a bath consisting mainly of  $\text{NaPO}_3$ . No attempt was made to formulate the overall reaction.

The oxyanions discussed so far were those of group IVA, VA and VIA elements. Molten oxyanions of group VIIA elements on the other hand have hitherto received very little attention. The only electroanalytical investigations reported concern the double layer capacity of the mercury - electrolyte interface in molten  $\text{LiClO}_4^-$   $\text{NaClO}_4$  (21), the formation of the chloride complexes of lead and cadmium in molten  $\text{LiClO}_4$  (22) and the solubility product of silver halides in molten  $\text{LiClO}_4$  (23). The authors of the last paper used a Ag(I)/Ag(O) reference electrode and showed that the Ag(I)/Ag(O) couple displayed



Nernstian behavior in molten LiClO<sub>4</sub> when Ag(I) was added as AgNO<sub>3</sub>. No direct coulometric generation of Ag(I) from silver was apparently attempted.

The only study of the electrochemistry of the solvent LiClO<sub>4</sub> itself was made by Johnson and Denning (24). These authors observed gas evolution on passage of current at a platinum cathode together with the deposition of black material. They also mentioned the explosive tendency of the cathode compartment which they ascribed to elementary lithium being formed behind an oxide layer and coming into contact with molten lithium perchlorate when the oxide layer fell away.

Apart from the molten state LiClO<sub>4</sub> has been the object of studies in organic media. Maki and Geske (25) electrolized a 0.1 M solution of LiClO<sub>4</sub> in acetonitrile and obtained from the anode compartment an ESR signal which they assigned to a ·ClO<sub>4</sub> radical. Both Cl<sup>35</sup> and Cl<sup>37</sup> have a nuclear spin of 3/2 which, in the case of the ·ClO<sub>4</sub> radical, gives rise to four equally spaced lines. No Hyperfine structure due to the two different chlorine nuclei was observed because of line broadening. The number of radicals present in a steady state at an electrolysis current of 3 mA was estimated at  $5 \times 10^{16}$  spins. The radical was scavenged finally by the solvent with regeneration of the ClO<sub>4</sub><sup>-</sup> anion.



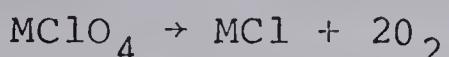
Cauquis and Serve (26) reinvestigated the electrolysis of LiClO<sub>4</sub> in the different solvent nitromethane and essentially confirmed the earlier results of Maki and Geske.



EXPERIMENTALSolvent

The perchlorates of group IA elements and ammonium are white crystalline solids.  $\text{LiClO}_4$  alone has a well defined melting point. The others decompose upon melting or within a very short temperature range of the melting point.

The heats of formation of the metal perchlorates are very nearly the same as the heats of formation of the corresponding chlorides (27). The reaction



thus takes place with little net energy change (27).

Lithium perchlorate stands out among the perchlorates as being the only one that is stable in the molten state. It melts without decomposition at  $247^\circ\text{C}$  and does not begin to show an appreciable decomposition rate until the temperature is raised over  $400^\circ\text{C}$  (28). All experiments reported in this part were done at  $260^\circ\text{C} \pm 10^\circ\text{C}$ .

$\text{LiClO}_4$  is fairly hygroscopic. Its molar heat of hydration (29) is 14.2 kcal/mole and the water of hydration is extremely difficult to remove. Berglund and Sillen (30) found that some water remained in the sample held at  $300^\circ\text{C}$  for 12 hours. The  $\text{LiClO}_4$  used in the present study was anhydrous reagent grade (Amend



Chemical Company). While it was dried under high vacuum for 3 days at 150°C, 100 - 150 ml of water were collected per kilogram melt. The procedure of drying the salt below its melting point was found to be more effective (31) than trying to remove the water from the melt. It was then melted and purged with dry chlorine for 30 minutes to remove any remaining oxidizable impurities (32); during this time the original dark melt became completely clear. This process was followed by nitrogen purging for 12 hours in order to remove the chlorine from the system. During the experiments nitrogen purging was kept up at a slow rate in order to keep the melt free from traces of water. The initial chloride content was in the range of  $2 \times 10^{-4}$  moles/kg melt. It did not increase to more than  $1 \times 10^{-2}$  moles/kg melt during the time of the investigations as shown by argentometric titration.

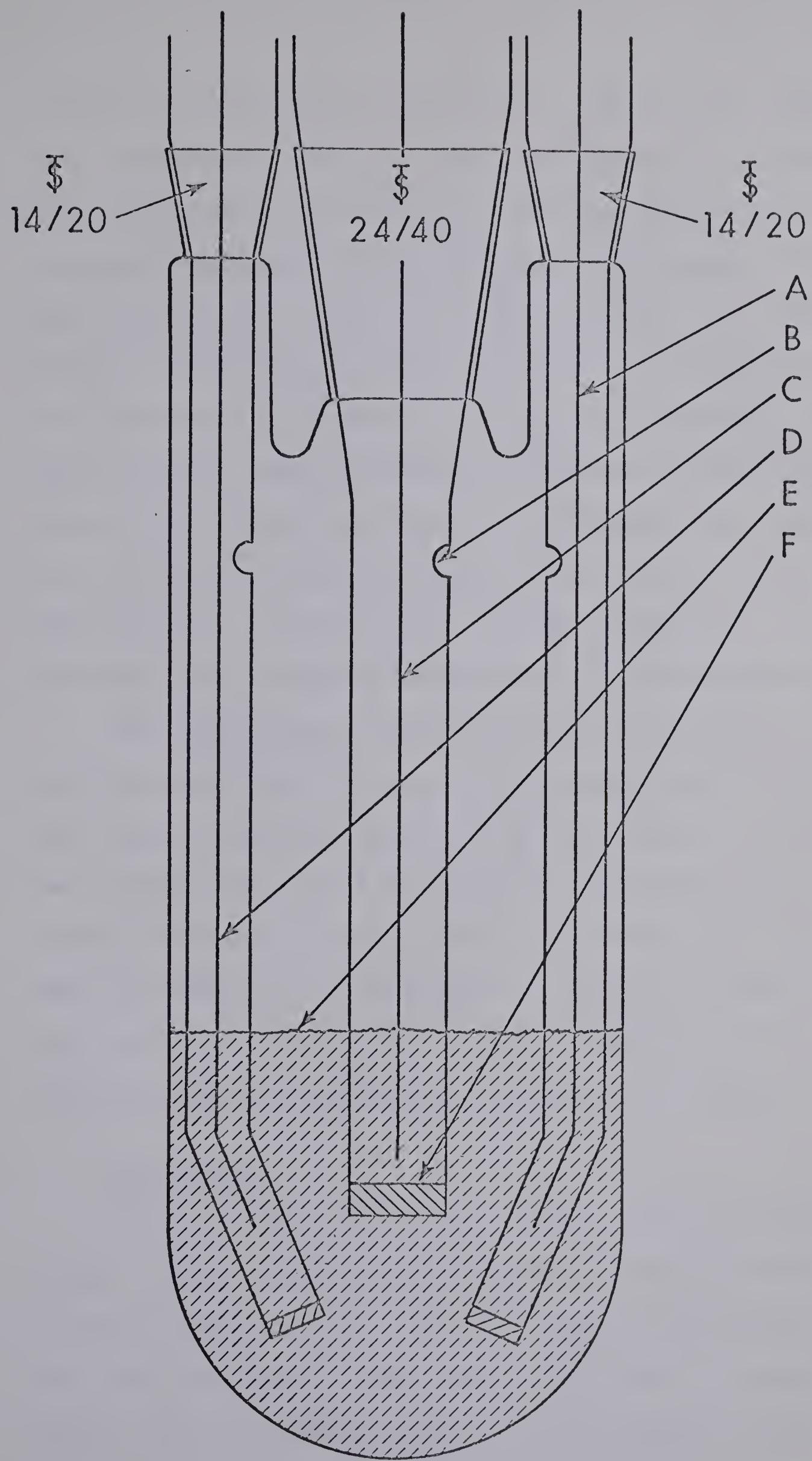
#### Apparatus

The cell (Figure 1) consisted of a Pyrex vessel with 24/40 and 14/20 standard taper joints. Pyrex feed-through tubes to which sintered glass disks of D porosity (Ace Glass Co., Vineland, N.J.) were fused served as isolation compartments. Holes in the feed-through wall above the melt level maintained equal pressure between the compartments and cell. The electrodes, each of which was kept in a separate isolation compartment, were silver wires

FIGURE 1

Fused Perchlorate Cell

- A, silver wire (reference electrode);
- B, pressure equalization vent;
- C, metal wire for anodization, or micro-electrode;
- D, silver wire (working electrode);
- E, melt surface;
- F, porous glass disk.





(reference and working electrodes), other metal wires (for anodization studies), and platinum microelectrodes. The heating unit consisted of a heating mantle and a heating tape regulated by variable transformers. For mass spectrometric samples, a Pyrex U-type cell (Figure 2) was constructed in which the anode and cathode compartments were separated by a sintered glass disk. The two electrodes were connected to tungsten leads sealed through the compartment tops. The cathode was a massive silver electrode while platinum served as the anode. Tubes leading through liquid nitrogen traps to a vacuum manifold were connected to both electrode compartments.

The voltammetric scans were performed with an Anotrol Model 4100 Potential Controller (Magna Electronics) using a platinum microelectrode, sealed in glass and ground flush, of  $0.9 \text{ mm}^2$  geometrical area. An Anotrol 4510 Scan Unit was used in combination with a EUW-20A (Heath Co.) multispeed recorder. A model IV Coulometric Current Source (E. H. Sargent and Co.) was used for the anodization of metal electrodes.

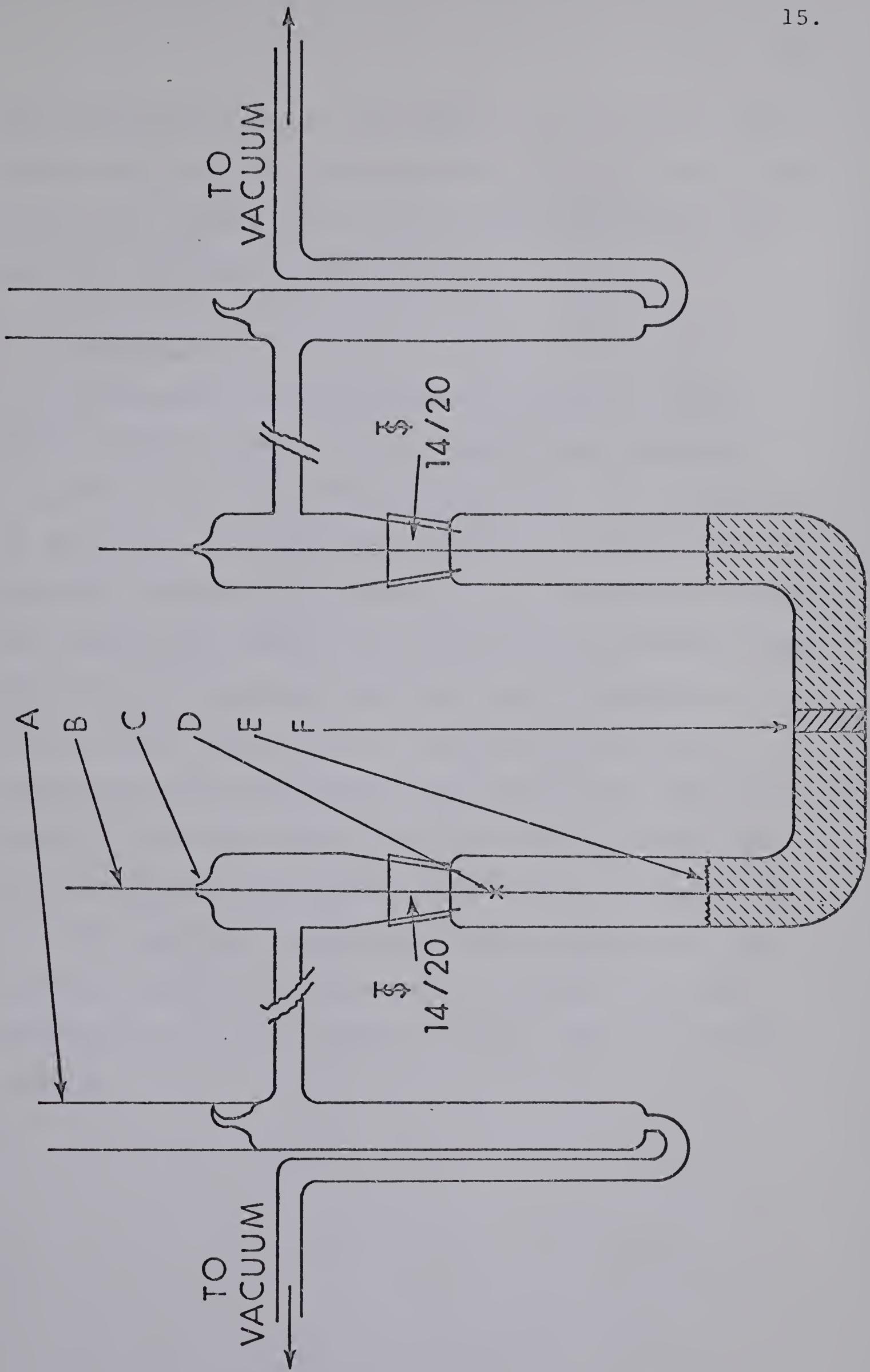
#### Chemicals

The  $\text{Li}_2\text{O}$  (Alfa Inorganics, Inc.),  $\text{Na}_2\text{O}_2$  (calorific grade, Allied Chemical),  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  (reagent grade, G. F. Smith Chemical Co.), and KOH (analytical grade, British Drug Houses) were used as received. Samples of  $\text{LiNO}_3$  (Alfa Inorganics, Inc.),  $\text{KClO}_3$  (reagent grade,

FIGURE 2

U-type Cell

- A, mass spectrometer tube;
- B, tungsten wire;
- C, seal;
- D, connection from tungsten to electrode metal;
- E, melt surface;
- F, porous glass disk.





Nichols Chemical Co.), and  $\text{KHSO}_4$  (reagent grade, Fisher Scientific) were vacuum-dried over magnesium perchlorate before use. Metal wires were cleaned mechanically and dried with acetone before use.

### Procedure

A reference electrode based on the  $\text{Ag(I)}/\text{Ag(O)}$  couple (about 0.2 molar or 0.1 molal) was generated coulometrically for each experiment, and all potentials in this paper are given with reference to this electrode. Nernstian behavior corresponding to a one-electron change was observed for silver in this solvent on oxidation and reduction, in agreement with the work of Bombi and co-workers (23). Oxide was determined by acidimetric titration of the hydroxide formed after hydrolysis of the contents of a compartment, and chloride was determined by conventional argentometric titration. The method of Chen (33) was used to determine small amounts of  $\text{ClO}_3^-$  in the presence of large amounts of  $\text{ClO}_4^-$ ; the same method indicated the absence of  $\text{ClO}_2^-$  and  $\text{ClO}^-$  in all samples.



R E S U L T S   A N D   D I S C U S S I O N

Voltammetric scans of the pure LiClO<sub>4</sub> melt with a platinum microelectrode gave the curve shown in Figure 3. At the anode the limiting electrode reaction occurs at +1.7 v, the rising portion being spread out over approximately 0.3 v. The cathodic limiting reaction occurs at -2.7 v. There is an additional cathodic peak at -1.5 v.

The cathodic limiting reaction is the deposition of lithium metal. Since pure lithium metal reacts explosively with the lithium perchlorate solvent (24) and since cathodic lithium deposition was inevitable during the investigation, it was necessary to reduce the activity of the lithium formed to as low a value as possible. It was found that alloy formation with silver served well for this purpose provided large enough silver electrodes and low enough current densities were used; current densities were approximately 0.1 amp/cm<sup>2</sup> and the total charge approximately one meq/cm<sup>2</sup>. This alloy formation reduced but did not completely halt the reaction between lithium and the melt; gentle gas evolution was continuous and the amount of lithium found in the silver was less than that calculated from coulombs passed. Platinum and tungsten electrodes did not show as large a capacity for lithium metal and explosions occurred with both.



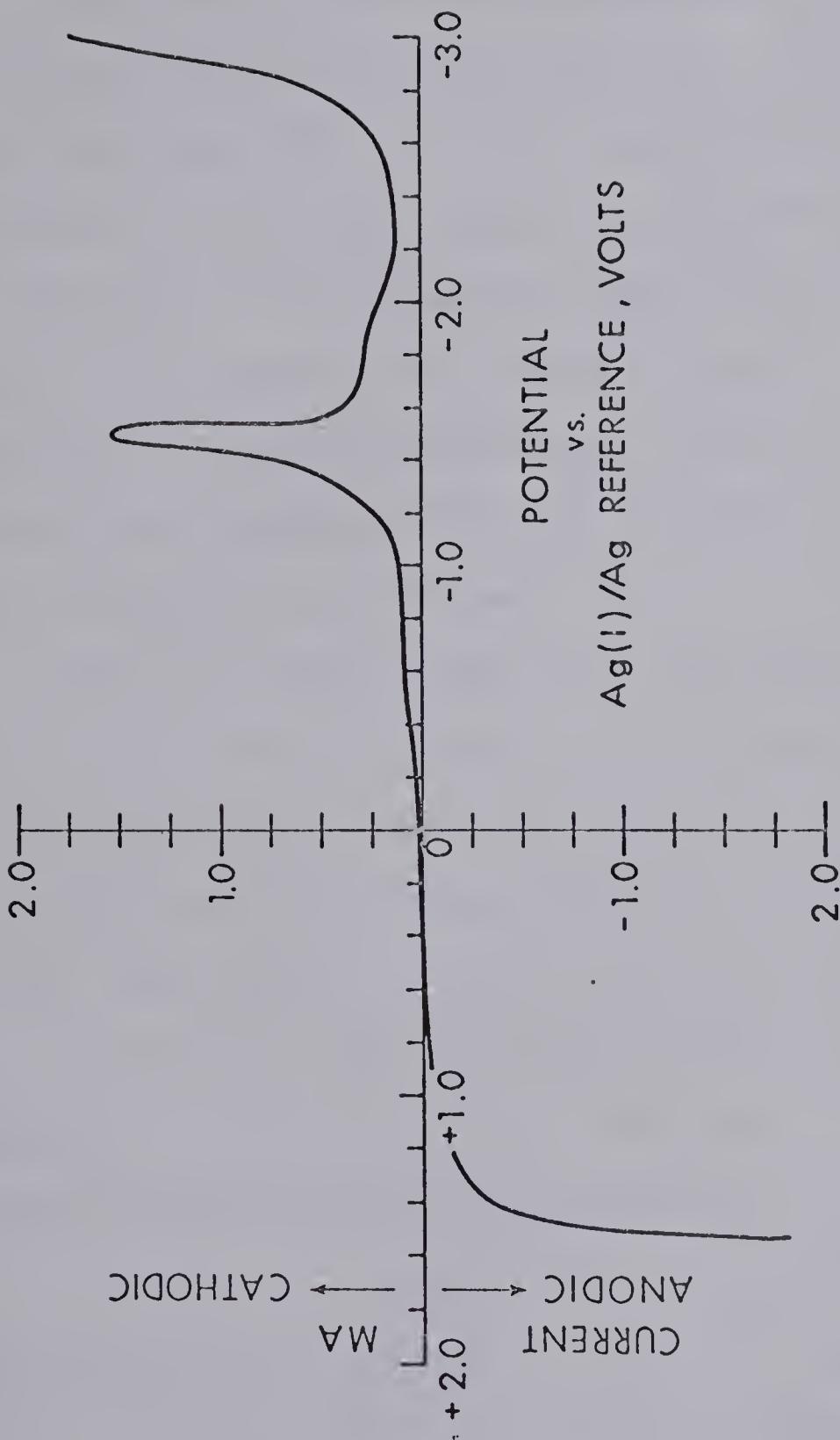
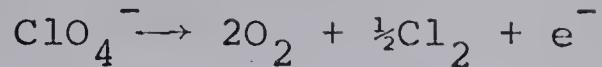


Figure 3. Voltammogram of fused lithium perchlorate. Platinum microelectrode, geometrical area  $0.9 \text{ mm}^2$ .



The overall process for the anodic limiting reaction appears to be



The slow curvature of the voltammogram as the anodic limiting process begins to occur may indicate an irreversible reaction (34) or other complication. The gases produced at the anode during electrolysis of pure LiClO<sub>4</sub> in the U-type cell (Figure 2) were pumped off under vacuum and trapped with liquid nitrogen. Mass spectrometric analysis on a MS-9 spectrometer (Associated Electrical Industries) showed no fragments containing Cl-O bonds. Only chlorine was detected.

There is a very small but reproducible wave at E<sub>1/2</sub> = -0.5 v, which by analogy with nitrate systems (35) is probably due to residual traces of water. Except for this, the only voltammetric feature visible between the anodic and cathodic limiting reactions was a cathodic peak at -1.5 v. This appeared similar to the peak observed in fused nitrates. The nitrate peak was interpreted (6,8,9) as due to the process



In nitrate melts the ratio e<sup>-</sup>:NO<sub>3</sub><sup>-</sup>:O<sup>2-</sup> was found to be 2:1:1. In a perchlorate melt the analogous process would be



When compartments of fused LiClO<sub>4</sub> were electrolyzed at



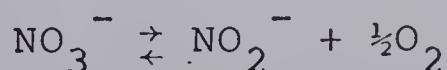
the peak potential of -1.5 v, the  $e^- : O^{2-}$  ratio found was 2.1 (std. dev. 0.2) to 1.0. No reproducible  $e^- : ClO_3^-$  ratio was observed, although comparison of the IR spectra (Perkin-Elmer 337, Nujol mull) of electrolyzed and un-electrolyzed  $LiClO_4$  revealed a new band at  $970\text{ cm}^{-1}$  which (by comparison with a known sample of  $KClO_3$ ) is due to the  $ClO_3^-$  ion (36). Chloride ion was also always present as shown by reaction with silver nitrate.

Attempts were made to determine the source of the peak by addition of reagents. Addition of  $H^+$  (as  $KHSO_4$ ) or  $OH^-$  (as KOH) produced no apparent change in the peak. Addition of  $ClO_3^-$  (as  $KClO_3$ ) also produced no change in the peak, indicating that it could not be due to the reaction

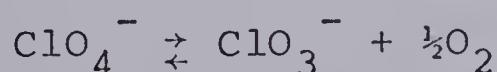


in fact, this reaction does not seem to occur within the decomposition range of the melt. Addition of  $H_2O$  (as  $LiClO_4 \cdot 3H_2O$ ) showed a small increase in the peak and violent evolution of water vapor.

The similarity between the cathodic peak observed in this study and those observed in nitrate melts (6,8) suggested the possibility of similar thermal equilibria in nitrate and perchlorate melts,

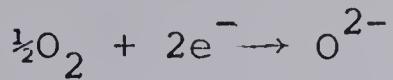


and





both producing oxygen. The dissolved oxygen formed might then be the material which undergoes electrochemical reduction,



explaining the 2:1 electron:oxide ratio. However, although addition of  $NO_3^-$  (as  $LiNO_3$ ) increased the cathodic current in the peak region, careful examination indicated that the  $NO_3^-$  and  $ClO_4^-$  peaks were different although quite close in potential (Figure 4), so that they in fact correspond to different processes. These peaks are not, then, due to dissolved oxygen. To prove this, the melt was saturated with dry oxygen gas; this had no effect on the height or position of the peak.

The major difficulty in the assignment of the peak to the



reaction was clearly that no consistent  $e^-:ClO_3^-$  ratio was found for the electrolysis of fused  $LiClO_4$ , unlike the nitrate melts in which the expected 2:1 ratio was obtained. Chlorate was always present but generally in amounts less than expected (Table I). Decomposition of the perchlorate solvent would cause inconsistent  $e^-:ClO_3^-$  ratios as observed, chlorate being an intermediate in the decomposition, and also account for the observed chloride. Since the expected ratio of  $e^-:O^{2-}$  was obtained, oxide could not be



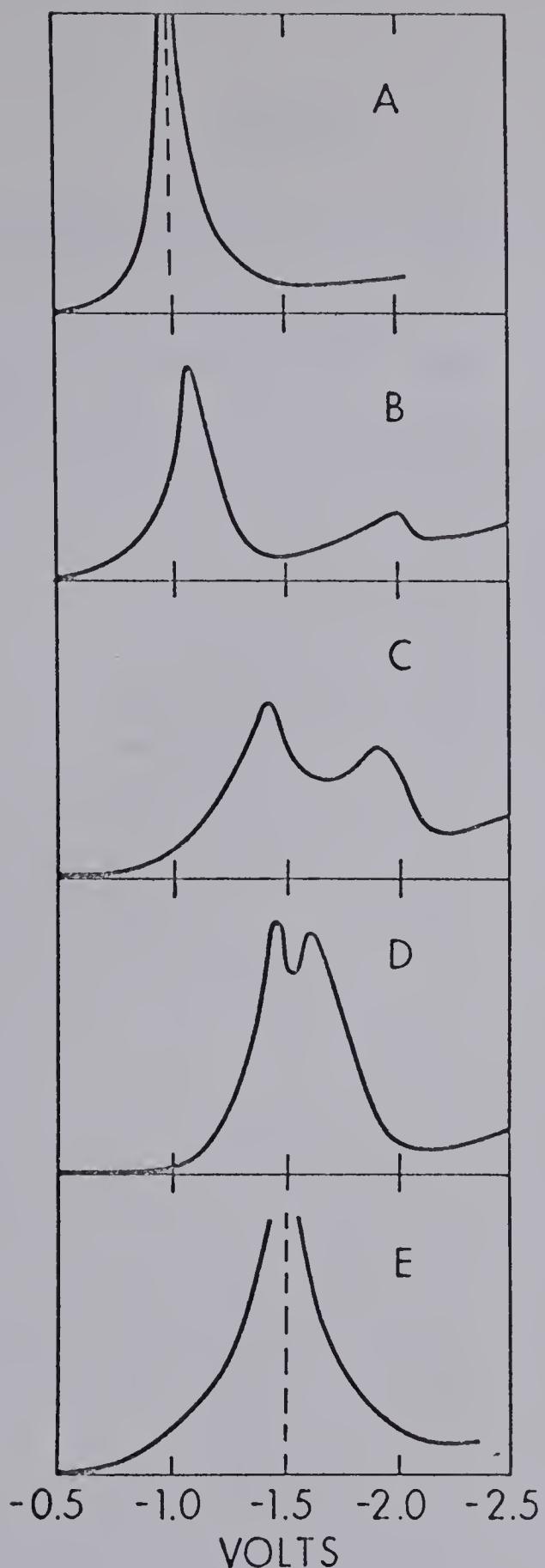


Figure 4. Voltammetric peak detail. A, pure  $\text{LiNO}_3$ ; B, C, D,  $\text{LiClO}_4$  with decreasing amounts of  $\text{LiNO}_3$ ; E, pure  $\text{LiClO}_4$ .

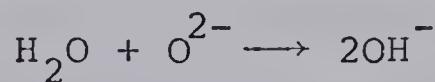


TABLE I  
STOICHIOMETRY OF CATHODIC PEAK

mequivalents electricity	mmoles OH <sup>-</sup>	mmoles ClO <sub>3</sub> <sup>-</sup>	mmoles Cl <sup>-</sup>
0.34		0.024	
0.90		0.023	
0.013		0.012	
3.3	2.9		1.6
3.4			3.0
3.4			4.1
3.1	2.8		1.7
1.8			0.38
1.7	1.8	1.25	0.27
1.4	1.2	0.29	0.22
1.8	2.0	0.70	0.31
1.8	1.8	3.7	0.28
0.26	0.27		0.040



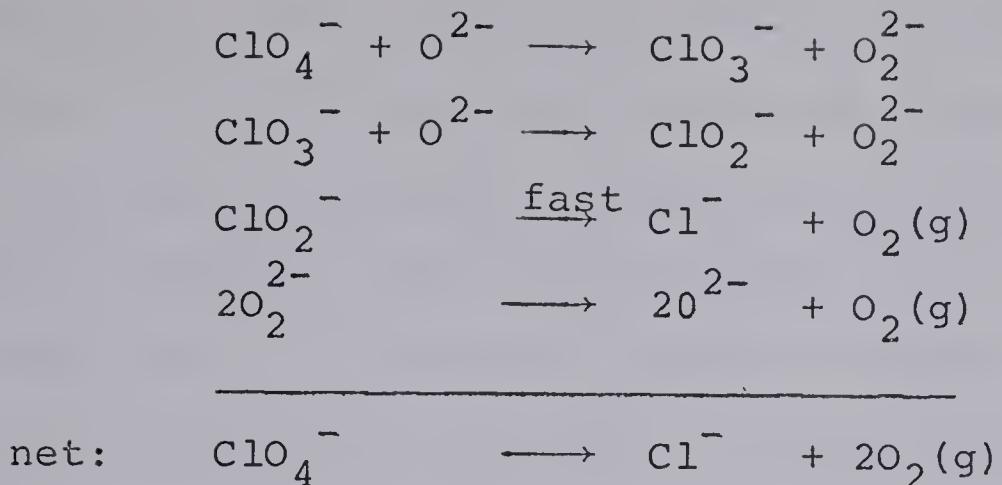
generated or used by this decomposition process; if involved, oxide must act as a catalyst. The gas evolved during electrolysis is therefore the oxygen produced by the oxide-catalyzed decomposition of chlorate and perchlorate to chloride. To test this,  $O^{2-}$  was added (as  $Li_2O$ ); obvious decomposition began at once and continued for at least 12 hours. Since the addition of  $OH^-$  (as KOH, which seems highly soluble in fused  $LiClO_4$ ) did not induce the catalytic decomposition, water was added (as  $LiClO_4 \cdot 3H_2O$ ) to samples in which obvious decomposition was occurring. Gas evolution ceased immediately, as would be expected if the decomposition were oxide-catalyzed; the addition of water would remove the oxide:



Additional evidence for an oxide-catalyzed decomposition is that the freshly generated oxides of magnesium and aluminum produced as discussed below also catalyzed melt decomposition although to a much lesser degree. It is well known that addition of metal oxides produces decomposition of both chlorate and perchlorate melts to chloride (28,37,38).

The catalytic decomposition which sets in after the  $O^{2-}$  is formed could occur by the following mechanism:





The postulated peroxide intermediate has been found in heated samples of  $\text{LiClO}_4\text{-Li}_2\text{O}$  by Markowitz and Boryta (28). Addition of peroxide (as  $\text{Na}_2\text{O}_2$ ) to the  $\text{LiClO}_4$  melt induced immediate obvious decomposition as expected. It was also demonstrated that the reaction



does not occur at an appreciable rate in the absence of oxide at this temperature; the addition of 250 mg of  $\text{KCLO}_3$  to a compartment containing approximately 5 g of fused  $\text{LiClO}_4$  did not result in any chlorate decomposition at  $260^\circ\text{C}$  after six hours, as shown by analysis.

A peculiarity of fused  $\text{LiClO}_4$  is that other than silver no metals could be anodized to form the corresponding ions. The fact that metals cannot be anodized into solution has also been found in the case of the nitrate melts. By addition of transition metal nitrates and chlorides to a nitrate melt a few metal ions could be brought into solution (39). This approach was not



possible in fused  $\text{LiClO}_4$ ; all added transition metal nitrates or chlorides produced oxides immediately. Some of the metal-metal oxide couples are of relatively stable potential; for example Mg/MgO at -2.1 v with a fluctuation of 40 mv over a period of hours. Some typical potentials of metals in contact with  $\text{LiClO}_4$  melt are listed in Table II.

Most metals form visible oxide layers with the exception of rhodium, iridium, and platinum which do not appear to form oxide layers even at high current densities. The behavior of the different metals tested is summarized in Table II. The behavior of thallium was unusual; the area of metal exposed to air formed black oxide as expected, while the area of metal exposed to the melt remained bright. On anodization, thallium was visibly lost from the wire, the surface remaining bright. Nernstian behavior was not observed; the potentials assumed after successive anodizations were stable but no reproducible Nernst slopes could be obtained, values of  $n$  ranging from 1.6 to 2.9. Analysis of the hydrolyzed melt for thallium (40) gave an  $e^-:\text{Tl}$  ratio of about 1:1. This behavior would suggest the formation of a thallium oxide soluble in fused lithium perchlorate.

The reason for this oxide formation with most



TABLE II  
METAL BEHAVIOR IN FUSED LITHIUM PERCHLORATE

Metal	Potential against Ag(I)/Ag (volts)	Oxide Formation (without current)	Oxide Formation (with current)
Mg	-2.1	massive	massive
Al	-0.4	film	massive
Ti	unstable	film	film
V	unstable	film	massive
Fe	unstable	massive	massive
Co	+0.4	massive	massive
Ni	+0.4	massive	massive
Cu	unstable	massive	massive
Zn	-0.7	massive	massive
Zr	unstable	film	massive
Nb	unstable	film	massive
Mo	unstable	film	massive
Rh	unstable	none	noble
Pd	unstable	thin film	film
Ag	0.0(def.)	none	forms Ag <sup>+</sup>
Cd	-0.5	massive	massive
W	unstable	film	film
Re	unstable	dissolves	dissolves
Ir	unstable	none	noble
Pt	unstable	none	noble
Au	unstable	none	thin film*
Hg	unstable	none	massive
Tl	-1.4	none	see text
Pd	-1.0	massive	massive
U	unstable	massive	massive

\* only at high current density; otherwise noble.



metals could well be the lower solvation energy of metal ions in fused perchlorates (and presumably also fused nitrates) as compared with fused chlorides (41) in which anodization of many metals is successful. To gain stabilization which is not available from the poorly-coordinating perchlorate anion, the metal cation presumably adds oxygen by breaking Cl-O bonds in a neighboring  $\text{ClO}_4^-$  anion.



C O N C L U S I O N

The electrochemical behavior of LiClO<sub>4</sub> is analogous to that of other molten salts containing oxyanions i.e., it showed in addition to the anodic and cathodic limiting reactions an additional cathodic peak. The reaction at this peak was shown to be



The generated oxide attacked the ClO<sub>4</sub><sup>-</sup> anion, contrary to the stability of oxide ion in other oxyanion melts. A peroxide intermediate was proposed for the decomposition of ClO<sub>4</sub><sup>-</sup> to chloride.

The cathodic peak reaction superimposed on the cathodic limiting reaction when the cathode was at the limiting potential. The lithium oxide produced shielded the simultaneously deposited lithium metal from solvent attack. Interruption of the current reduced the lithium oxide concentration in the immediate vicinity of the electrode and the lithium metal reacted vigorously with the solvent. Alloying with silver metal electrodes prevented this spontaneous reaction between lithium metal and the perchlorate ion.

No reversible metal ion/metal couples besides silver could be realized. This was explained by the poor coordination stabilization given by the perchlorate anion. The metal ions will break Cl-O bonds and become



stabilized by oxide ions. This behavior of metal ions greatly diminishes the usefulness of lithium perchlorate as a solvent in electrochemical investigations. Furthermore, oxide ions from the glass containers decomposed the melt slowly, which resulted in a continuous increase in the chloride concentration. This makes the solvent unfit even for a study of chloride complexes.



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PART IITHE ELECTROCHEMISTRY OF GROUP IB AND IIIA METALS IN  
FUSED  $\text{AlCl}_3\text{-NaCl-KCl}$  EUTECTICA B S T R A C T

The electrochemistry of copper, silver, gold, gallium, indium, thallium and their ions, and of chlorine and bromine in fused  $\text{AlCl}_3\text{-NaCl-KCl}$  was investigated by e.m.f. and voltammetric techniques. Univalent oxidation states were observed for all of the metals. In addition, copper was further oxidized to the divalent species while gallium and indium were oxidized to trivalent species. The standard potentials for the above couples were established in the  $\text{AlCl}_3\text{-NaCl-KCl}$  eutectic at 135°C.



## INTRODUCTION

Despite the fact that aluminum metal has been produced electrochemically for over 80 years little effort has been directed towards a systematic study of the haloaluminate melts. The understanding of the physical chemistry and electrochemistry of the fluoroaluminates and the chloroaluminates is far from being complete (1). While the fused fluoroaluminates are of great importance in the production of aluminum (1), it has recently been found (2-12) that chloroaluminate melts have a surprisingly strong tendency to stabilize low valence states of metals.

This behavior will be the concern of this and the following part of this thesis. Part II deals especially with the electrochemical generation and characterization of low valence states of group IB and IIIA metal ions in the ternary  $\text{AlCl}_3\text{-NaCl-KCl}$  eutectic. The physical data of this system have been summarized in detail before (3) and will not be repeated here.

L. F. Yntema and coworkers (13-17) were the first to investigate the possibilities of the ternary  $\text{AlCl}_3\text{-NaCl-KCl}$  eutectic as a solvent for metal ions 25 years ago. The low melting point of this eutectic was first found by Wasilewski, Kaczorowski and Dynkin in 1934 (18).

Yntema's first paper (13), however, led to



erroneous conclusions because of the reference electrode used. It consisted of a platinum wire inserted into the melt. It was argued that the sum of the potential drops from anode to reference electrode and reference electrode to cathode was equal to the potential difference between anode and cathode. Then the reference electrode to cathode potential drop, as extrapolated to zero current, was assumed to be determined by the reaction at the cathode.

While this argument is basically correct, a reference electrode of this type has severe practical disadvantages. The main objection comes from the undetermined potential at which the reference electrode is held. The potential determining species will be melt impurities and therefore probably be of low concentrations. An electrode of this type will be very susceptible to concentration polarization, even at very low current densities. A further disadvantage of a reference electrode of this type is that the reference electrode will not necessarily be stable even at negligible polarization from one experiment to the other nor will it be reproducible in another run. Consequently, the discrepancies between the deposition potentials quoted in the first paper (13) and the following (14), in which he used the now well-established Al(III)/Al(O) (2,3) reference electrode, were quite large; e.g., for copper 0.85 V (13) and 0.66 V (14).



Yntema's interests apparently lay mainly in the electro-deposition of metals from their ions dissolved in chloroaluminate melts, and little attention was paid to other effects. In group IB he studied the deposition of copper from added CuCl (13,14) and of silver from added AgCl (14). In group IIIA gallium was deposited from a solution of  $\text{Ga}_2\text{O}_3$  in the ternary eutectic (17). Although TlCl was dissolved in the bath (17) he observed neither oxidation nor reduction of the Tl(I) which led him to the erroneous conclusion that TlCl must be highly insoluble in the melt eutectic.

While this thesis agrees basically with Yntema's findings in the case of group IB, it was found that Yntema's interpretation concerning group IIIA metals and their ions were not correct. It was not known at this time that gallium has a stable plus one oxidation state. Accordingly, when Ga(III) was added to the melt and gallium deposited at the cathode the presence of Ga(I) as an intermediate was not recognized although the current voltage curve displayed one well-defined additional break at high current densities. It is now known that gallium metal reacts with gallium trichloride to form  $\text{Ga}[\text{GaCl}_4]$ , a complex containing equal amounts of Ga(I) and Ga(III). Excess gallium metal does not undergo further reaction with this complex unless aluminum trichloride is added (19); under these circumstances the  $\text{GaCl}_4^-$  ion reacts until all Ga(III) is

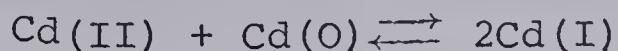


reduced to Ga(I). The resulting complex has the formula  $\text{Ga}[\text{AlCl}_4]$ .

Thallous chloride, as will be shown later, is soluble in the melt contrary to Yntema's conclusions but it is not electrochemically active.

The metals investigated in this study were those of group IB and IIIA, thus extending the previous work in this field done by D. A. Hames and J. A. Plambeck (2, 3). The latter authors have shown (2,3) that in the ternary  $\text{AlCl}_3\text{-NaCl-KCl}$  zinc exists in the plus two oxidation state while cadmium and mercury exist in both the plus one and plus two oxidation states. The electrochemical techniques of potentiometry, voltammetry and chronopotentiometry were used to study dilute solutions of these ions.

The numerical findings of Hames and Plambeck (2,3) were highly precise. But several disagreements between different investigators seem to exist. The value of the equilibrium constant for example of the reaction



was reported by Hames and Plambeck as  $3.6 \times 10^4$ . Corbett and coworkers (7) found a value of  $1.71 \pm 0.11$  on the basis of spectroscopic studies. However, solvent and temperatures used were not identical in the two studies. While Hames

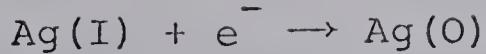


and Plambeck used the ternary  $\text{AlCl}_3\text{-NaCl-KCl}$  eutectic (66 mole %  $\text{AlCl}_3$ , 20 mole %  $\text{NaCl}$ , and 14 mole %  $\text{KCl}$ ) at  $135^\circ\text{C}$ , Corbett and his group used the system  $\text{NaAlCl}_4$  - 7.7 mole %  $\text{AlCl}_3$  at  $350^\circ\text{C}$ . A qualitative interpretation of the differences would have to invoke the concept of acid stabilization (3,20,21) which will be presented in detail in Part III. Furthermore, it would be expected that the temperature difference of  $200^\circ\text{C}$  would also decrease the equilibrium constant observed by Hames and Plambeck because the thermal energy would weaken the metal-metal bond.

Another point of discrepancy is the zinc ion/zinc electrode. T.C.F. Munday (5) and the author of this thesis observed drifting potentials when zinc ions were produced by coulometric oxidation of zinc into the melt. Munday used the  $\text{NaAlCl}_4$  - 5 mole %  $\text{AlCl}_3$  system. Contrary to this, Hames and Plambeck (2,3) found the couple to be well-behaved. Their Nernst plot resulted in a straight line with a slope of  $n = 2$ . Their current densities used for the anodization were comparable to those of this thesis.

Discrepancies in the potentiometric data of the silver ion/silver electrode were found between this thesis and the work of Hames and Plambeck (2,3) and Corbett's school (4,5). This was very unexpected since no deviating behavior for the reaction





has been reported for  $\text{Ag(I)}/\text{Ag(O)}$  before in fused salts or other solvents. Indeed the  $\text{Ag(I)}/\text{Ag(O)}$  couple was the only one which could be realized in the fused  $\text{LiClO}_4$  system (22).

At this point the question of solvent purity and reproducibility arises. But as will be discussed later in detail it appears at the present time that melt impurities cannot be responsible for the observed behavior. Certain drifting potentials in molten chloroaluminates have been encountered by all workers (2-5) and in all cases this has had physical significance.

Corbett and his school (4) were the first to interpret the potential drifts in terms of complexation of the metal ions with one another. It has been shown that the  $\text{CdCl}_2/\text{Cd}$  system gave rise to subvalent cadmium species whose existence could be substantiated by magnetic (23), Henry's Law (24) and cryoscopic (25) studies as well as electrochemical methods (24,26). However, an uncertainty in the solute arises in all of these cases from the general inability to determine the amount of metal consumed in dilute solutions where ideal solution laws may be expected so apply. Only measurements concerning solute mobility (27,28) in this system suggest that the produced species is charged. On the other hand, a specific solute



is indicated by studies in the  $\text{CdCl}_2\text{-AlCl}_3$  system. Besides, the introduction of  $\text{AlCl}_3$  does not seem to alter the production of the subvalent species (4-6).

Reduction of divalent lead (4) resulted in a species  $\text{Pb}^+$  (indistinguishable with the experimental methods from  $\text{Pb}_2^{3+}$ ,  $\text{Pb}_3^{5+}$  etc.). In the case of tin the product of the reaction appeared to be  $\text{Sn}_2^+$  (again indistinguishable from  $\text{Sn}_2^{3+}$ ,  $\text{Sn}_4^{5+}$  etc.).

No rational explanation has so far been found for the drifting potentials in the case of the zinc electrode (5).

The bismuth ion has been studied extensively (6-12). The low valence states found corresponded to  $\text{Bi}^+$ ,  $\text{Bi}_4^{4+}$ ,  $\text{Bi}_5^{3+}$  and  $\text{Bi}_8^{2+}$ .

Austin, Vucick and Smith (29) suspected a Mn(I) species in a melt consisting of 80%  $\text{AlCl}_3$ , 10% NaCl and 10% KCl. It is, however, not clear from their text how the Mn(I) could have been generated from the added Mn(II). A reasonable interpretation might be that their anode consisted of aluminum metal which may then have reduced Mn(II) to Mn(I).



### E X P E R I M E N T A L

The electronic instrumentation and electrochemical cell used have been described previously (2). The metals for the electrode were obtained in wire form from A. D. MacKay (New York, N.Y.) and were of 99.99% purity. Anhydrous  $\text{GaCl}_3$  and  $\text{InCl}_3$  were produced from the pure metals and chlorine gas (30). Anhydrous  $\text{InCl}$  was purchased from Alfa Inorganics (Beverly, Mass.). Reagent grade  $\text{AlCl}_3$ ,  $\text{NaCl}$  and  $\text{KCl}$  (Fisher Scientific Co.) were used. The purification procedure used for the aluminum chloride in this investigation was less cumbersome than that previously reported (2) and allowed the preparation of a new melt for each experiment. In this procedure 250 g of aluminum chloride were placed in a closed-end Pyrex tube 40 cm long and 5 cm in diameter, which was fitted with a 6 cm O-ring joint. The aluminum chloride was covered with a 1 cm thick layer of granular aluminum metal (reagent grade 30 mesh, Fisher Scientific Co.). The tube was flushed with nitrogen and closed with a Pyrex cap which had a 4 mm stopcock on top; this was open to a mercury pressure relief valve during the sublimation. The vertical tube was heated by an external heating mantle and heating tape which extended to the height of the aluminum layer. A tubular ring with pin holes pointing inwards fitted loosely over the sublimation tube. Compressed air was blown through it to cool the tube and prevent condensation



of subliming aluminum chloride in the upper half of the tube. It was positioned approximately 10 cm down from the glass joint. The aluminum chloride condensed over a length of 7-10 cm as a colorless, crystalline solid. After nearly complete sublimation the closed tube was cooled and transferred into a glove box filled with dry nitrogen. The glass tube was then broken to obtain the solid aluminum chloride. The lower part of the crystallized aluminum chloride cylinder was generally discarded due to baked-in granular aluminum.

The aluminum chloride obtained by the above procedure was a crystalline material pure white in color. It was ground, transferred into a tightly stoppered flask, removed from the glove box, weighed and returned to the glove box in which all further work was done. After addition of the appropriate amounts of sodium chloride and potassium chloride, the mixture was melted in a round bottomed flask and transferred into the electrochemical cell previously described (2). It was observed that the color of the melt varied from a faint yellow to light brown with the temperature employed during this initial melting process. The cause of the coloration is unknown. It has been suggested that it is due to carbon from organic material (31,32) or dissolved silicon compounds (33). The present author has observed,



however, that chlorine or hydrogen chloride also produce melt darkening, and for that reason these gases could not be used in the melt purification.

An aluminum wire spiral was added to the melt for one hour in order to reduce any metal ion impurities.

#### Reference Electrode

All potentials were measured with respect to an aluminum wire inserted into the melt. The use and non-polarizability of this reference electrode have been described (2). All measurements were made at  $135^\circ \pm 1^\circ\text{C}$  rather than at  $150^\circ\text{C}$  (2), to keep evaporation of the aluminum chloride to a minimum during the experiments.

#### Metal-Metal Ion Electrodes

The compartments consisted of 10C sealing tubes (Ace Glass Inc., Vineland, N.J.) which were inserted into the melt and allowed to fill to the melt level. The metals were inserted as wires except in the case of gallium which is a liquid at this temperature. Here a spoon-like Pyrex cup was used which was attached to the end of a glass tube. A platinum wire which did not come in contact with the melt led to the bottom of the cup which was filled with liquid gallium metal and then inserted into the compartment.



### Gas Electrodes

The chlorine electrode employed a compartment consisting of a 10D sealing tube extended to 20 cm and closed on top. A tungsten wire was sealed through the top and reached to the frit, parallel to a glass tube of 5 mm O.D. which served as a feed-in tube for chlorine gas and which also entered the compartment near the top. A second tube on top of this half cell was used as a gas outlet. The chlorine gas was dried over phosphorus pentoxide before being fed through Teflon tubing to the electrode.

Chlorine gas was first bubbled through the melt rapidly to saturate the melt and displace the nitrogen above it. Then time was allowed for the melt to reach thermal equilibrium, until the potential became stable within 1 mV. It was ascertained by several more small additions of chlorine and successive equilibrations that the melt was truly saturated with chlorine gas.

The bromine cell differed from the above by an additional 10/35 standard taper joint on top into which a small dropping funnel containing liquid bromine was fitted. At first a total of 5 ml of bromine were added in small portions to saturate the melt with bromine as well as to replace the nitrogen above it by bromine vapor. Bromide ion was produced by coulometric reduction of bromine in the compartment at a tungsten electrode operated at low current densities. The melt was occasionally



checked for bromine saturation by addition of small amounts of bromine as described above for the chlorine electrode.



R E S U L T S   and   D I S C U S S I O N

In order to report standard potentials the standard states must be defined. The standard states used in this work are: gases, 1 atm. pressure; elements and compounds, pure element or compound in the most stable form at the temperature used; species which are melt constituents (or are linked to a melt constituent by a non-electrochemical equilibrium, such as Al(III), the form in which they actually exist in the pure melt; species which are not melt constituents, unit concentration on a specified concentration scale (e.g., one molar) but with the properties of the species at infinite dilution in the solvent melt. This definition agrees with those used for other melts (34). Under these conditions the standard and measured potentials of the Al(III)/Al(0) electrode are the same, and all standard or measured potentials in this paper are given with respect to this electrode. These potentials, on the molar, molal, and mole fraction concentration scales, are given in Table 1. All conform to the IUPAC "Stockholm" sign convention, and all have positive sign. tolerances given are standard deviations.

Chlorine

To establish the potential span of the melt in terms of standard potentials the e.m.f. of the  $\text{Cl}_2/\text{Cl}^-$  couple was measured precisely. Yntema and co-workers (13,14) reported a value of  $2.09 \pm 0.04$  V for this couple at  $156^\circ\text{C}$ .



TABLE I

Electromotive Force Series in  $\text{AlCl}_3\text{-NaCl-KCl}$  at 135°C

Couple	$E^\circ$ molar	$E^\circ$ molal	$E^\circ$ m.f.	standard div.
$\text{Al(III)}/\text{Al(0)}$	0.000	0.000	0.000	defined <sup>a</sup>
$\text{Ga(I)}/\text{Ga(0)}$	0.199	0.222	0.276	0.002
$\text{Zn(II)}/\text{Zn(0)}$	0.254 <sup>b</sup>	0.263 <sup>b</sup>	0.304 <sup>b</sup>	0.002
$\text{Ga(III)}/\text{Ga(0)}$	0.577 <sup>c</sup>	0.585 <sup>c</sup>	0.603 <sup>c</sup>	0.002
$\text{Cu(I)}/\text{Cu(0)}$	0.689	0.710	0.745	0.002
$\text{Ag(I)}/\text{Ag(0)}$	0.695	0.719	0.802	0.001
$\text{Ag(I)}/\text{Ag(0)}$	0.740 <sup>b</sup>	0.759 <sup>b</sup>	0.832 <sup>b</sup>	0.001
$\text{Ga(III)}/\text{Ga(I)}$	0.766	0.766	0.766	0.002
$\text{Hg(I)}/\text{Hg(0)}$	1.028 <sup>b</sup>	1.037 <sup>b</sup>	1.077 <sup>b</sup>	0.001
$\text{In(III)}/\text{In(I)}$	1.1	1.1	1.1	0.15
$\text{Hg(II)}/\text{Hg(0)}$	1.22 <sup>b,c</sup>	1.231 <sup>b,c</sup>	1.271 <sup>b,c</sup>	0.002
$\text{Cu(II)}/\text{Cu(0)}$	1.278 <sup>c</sup>	1.288 <sup>c</sup>	1.306 <sup>c</sup>	0.002
$\text{Hg(II)}/\text{Hg(I)}$	1.415 <sup>b</sup>	1.424 <sup>b</sup>	1.464 <sup>b</sup>	0.002
$\text{Br}_2/\text{Br}^-$	1.768	1.785	1.631	0.002
$\text{Cu(II)}/\text{Cu(I)}$	1.866	1.866	1.866	0.001
$\text{Au(I)}/\text{Au(0)}$	2.022	2.046	2.119	0.002
$\text{Cl}_2/\text{Cl}^-$	2.064	2.064	2.064	0.002

<sup>a</sup>defined as 0.000 at all temperatures in this melt.<sup>b</sup>measured at 150°C; Ref. (2)<sup>c</sup>calculated from free energies of experimentally measured couples.



Treadwell and Tereberi (35) found 2.062 V at 721 mm Hg and 135°C in a slightly different ternary system (62 mole %  $\text{AlCl}_3$ , 26 mole % NaCl and 12 mole % KCl). The temperature dependence, as measured vs. an Al(III)/Al(O) reference electrode, at a platinum electrode was -0.72 mV/°C. Kher and Mene (36), in using the  $\text{NaAlCl}_4$  system, found the temperature dependence of the anodic decomposition potential to be 0.982 mV/°C. The temperature range extended from 200 to 660°C. Graphite anodes and cathodes were used.

The present study reports a standard potential of  $2.064 \pm 0.002$  V at 135°C and 1 atm. The standard and measured potentials for the couple are the same under the standard state definitions given above. The temperature dependence of the electrode was measured from 120° to 180°C as  $-0.65 \pm 0.03$  mV/°C. No hysteresis was observed.

The potential separation on a molal basis of the Al(III)/Al(O) and  $\text{Cl}_2/\text{Cl}^-$  couples in the LiCl-KCl melt is 2.073 V with a temperature dependence of the  $\text{Cl}_2/\text{Cl}^-$  electrode vs. a Pt(II)/Pt(O) electrode of  $-0.334 \pm 0.008$  mV/°C (34,37). No direct comparison is possible between the values for the two standard potentials, however, due to the different definitions of the standard states of the Al(III) ions.

Identical potentials were obtained for chlorine in the  $\text{AlCl}_3\text{-NaCl-KCl}$  melt with carbon and tungsten electrodes.



It must be noted that the carbon electrodes disintegrated slowly upon contact with the melt to give carbon powder. This, however, did not give rise to an observable change in potential. Apparently this disintegration, which also occurs in the melt in the absence of chlorine, is due to the high content of aluminum trichloride since carbon electrodes have been used successfully in the  $\text{NaAlCl}_4$  melt (4). However, Russian reports (38) do mention disintegration of graphite electrodes in  $\text{NaAlCl}_4$ .

The observation that a briefly shorted chlorine electrode would return to the previous equilibrium potential inside a few seconds led to a closer investigation of this phenomenon. The cell used was as described previously with a 1/8 inch O.D. graphite electrode. The temperature of the cell was maintained at  $154 \pm 1^\circ\text{C}$ . Chlorine gas was passed over the electrode surface at an originally slow rate i.e., one bubble/5 seconds. The flow was speeded up to one bubble/second after 70 minutes when it became apparent that the gas flow could not keep up the potential (Figure 1). A 1 ohm resistor was connected across the cell and the voltage dropped across it was measured with a digital voltmeter. Figure 1 shows the current-time dependence of this cell.

The amount of electricity passed during this period was calculated as 187 coulomb. Using a value of 17.5 mA for an average current over the 3 hour period an average power dissipation of 0.3 mW results.



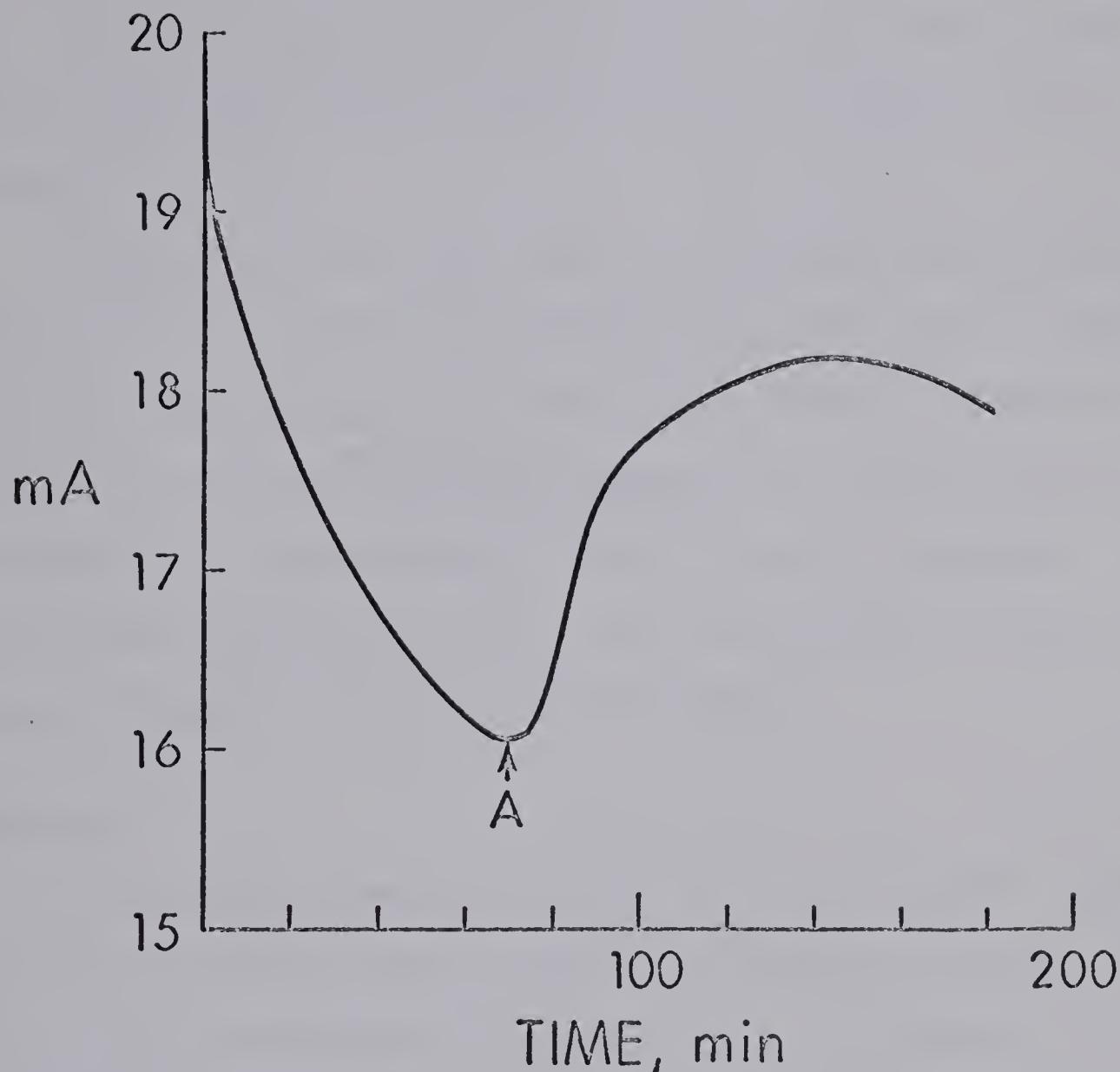


Figure 1. Time-current dependence of the chlorine fuel cell. At A the chlorine flow was increased fivefold.



The graphite electrode disintegrated nearly completely during the 3 hour period. It is for this reason that no exact current density can be given for the electrode. The original geometrical area was  $3.6 \text{ cm}^2$  which results in an estimated initial average current density of  $4.9 \text{ mA/cm}^2$ .

The above data show that the chlorine electrode has features which make it promising as a fuel cell. Since the aluminum electrode which serves as a counter electrode is highly reversible and since the Al(III) concentration is very high no polarization occurs at this electrode. The only polarization this fuel cell experiences is concentration polarization at the chlorine electrode.

#### Bromine

The molal standard potential of the  $\text{Br}_2/\text{Br}^-$  couple was found to be  $1.785 \pm 0.002 \text{ V}$  at  $135^\circ\text{C}$  and 1 atm. The temperature dependence of this couple was measured as  $-0.16 \pm 0.03 \text{ mV/}^\circ\text{C}$  from  $120^\circ$  to  $170^\circ\text{C}$ . From the published data on the bromine electrode (34,37) one can calculate the separation between Al(III)/Al(O) and  $\text{Br}_2/\text{Br}^-$  in the LiCl-KCl melt to be 1.897 V. The temperature dependence of the bromine electrode has not been established in the LiCl-KCl melt.

#### Gallium

Gallium metal was anodized at low current densities to form Ga(I) (Fig. 2). The Nernst plot indicated a slope



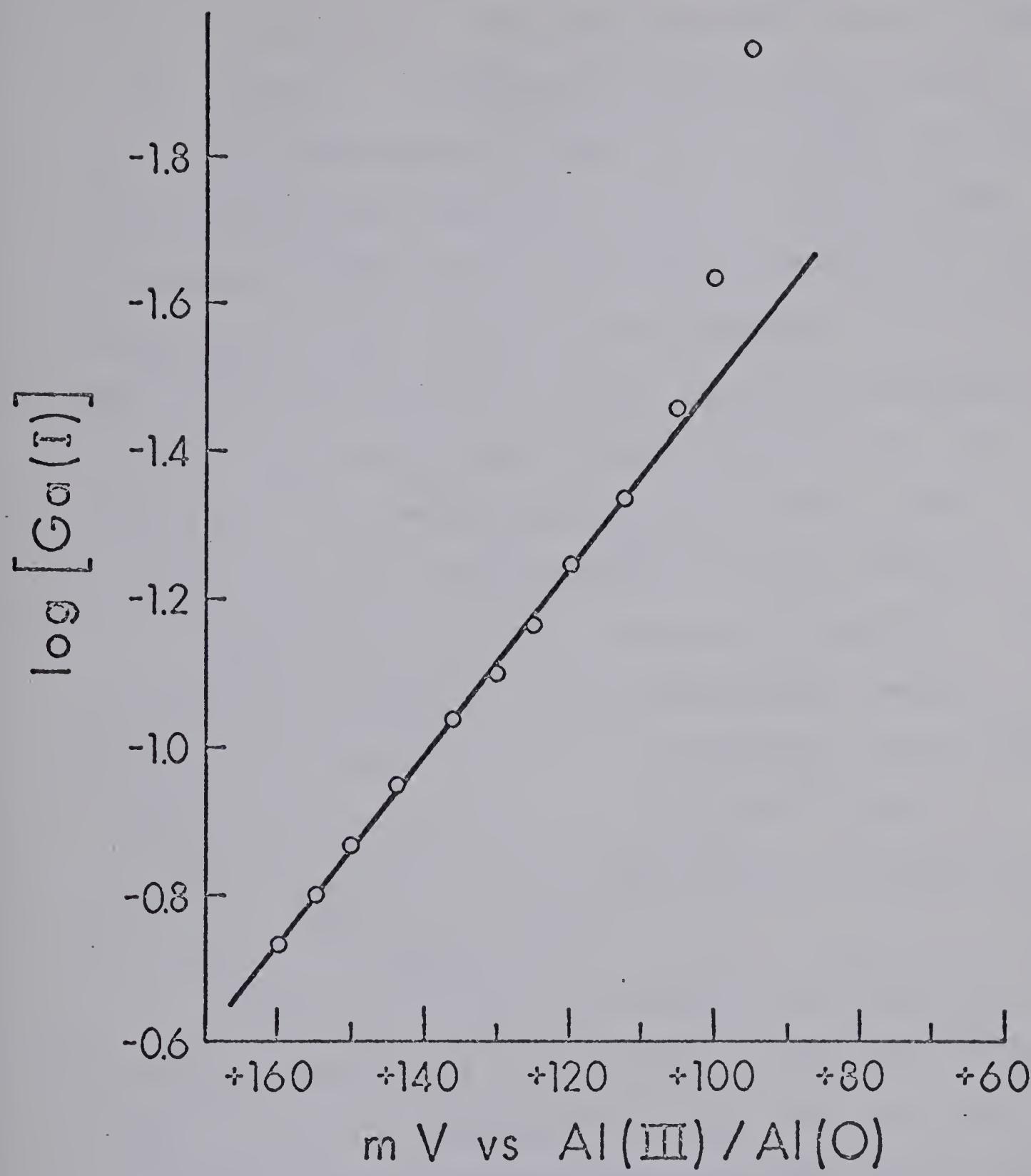


Figure 2. Nernst plot for the  $\text{Ga}(\text{I})/\text{Ga}(\text{O})$  couple.  
Typical run, concentration on molal basis.



of 81 mV/log unit for this process, corresponding to  $1.0 \pm 0.1$  electrons. The molal standard potential was  $0.222 \pm 0.002$  V. Voltammetry with an inert tungsten electrode indicated the presence of an anodic wave corresponding to the oxidation of Ga(I). Quantitative coulometric oxidation at a platinum electrode at  $5 \text{ mA/cm}^2$  showed this to be a two-electron process. The plot of  $\log [\text{Ga(I)}]/[\text{Ga(III)}]$  vs. e.m.f. (Fig. 3) resulted in a straight line whose slope corresponded to  $2.2 \pm 0.1$  electrons. A standard potential of  $0.766 \pm 0.002$  V was measured at equal concentrations of Ga(I) and Ga(III).

With these data it is possible to calculate the equilibrium constant. If the equilibrium reaction is defined as  $1/2\text{Ga(III)} + \text{Ga(O)} \rightleftharpoons 3/2\text{Ga(I)}$ , which involves a change of one electron,  $K = 5.0 \times 10^6$  (Table 2). The equilibrium constant is in molal units and given by  $K = [\text{Ga(I)}]^{3/2}/[\text{Ga(III)}]^{1/2}$ .

Figure 4 shows two voltammetric curves of gallium solutions which were obtained with a tungsten microelectrode. Curve A represents the result of a scan of a solution approximately 0.1 molal in Ga(I) while Curve B was obtained at equal concentrations of Ga(I) and Ga(III), about 0.5 molal.

Curve A, starting close to the Al(III)/Al(O) potential and scanning towards more oxidizing potentials, produces first a cathodic wave corresponding to the



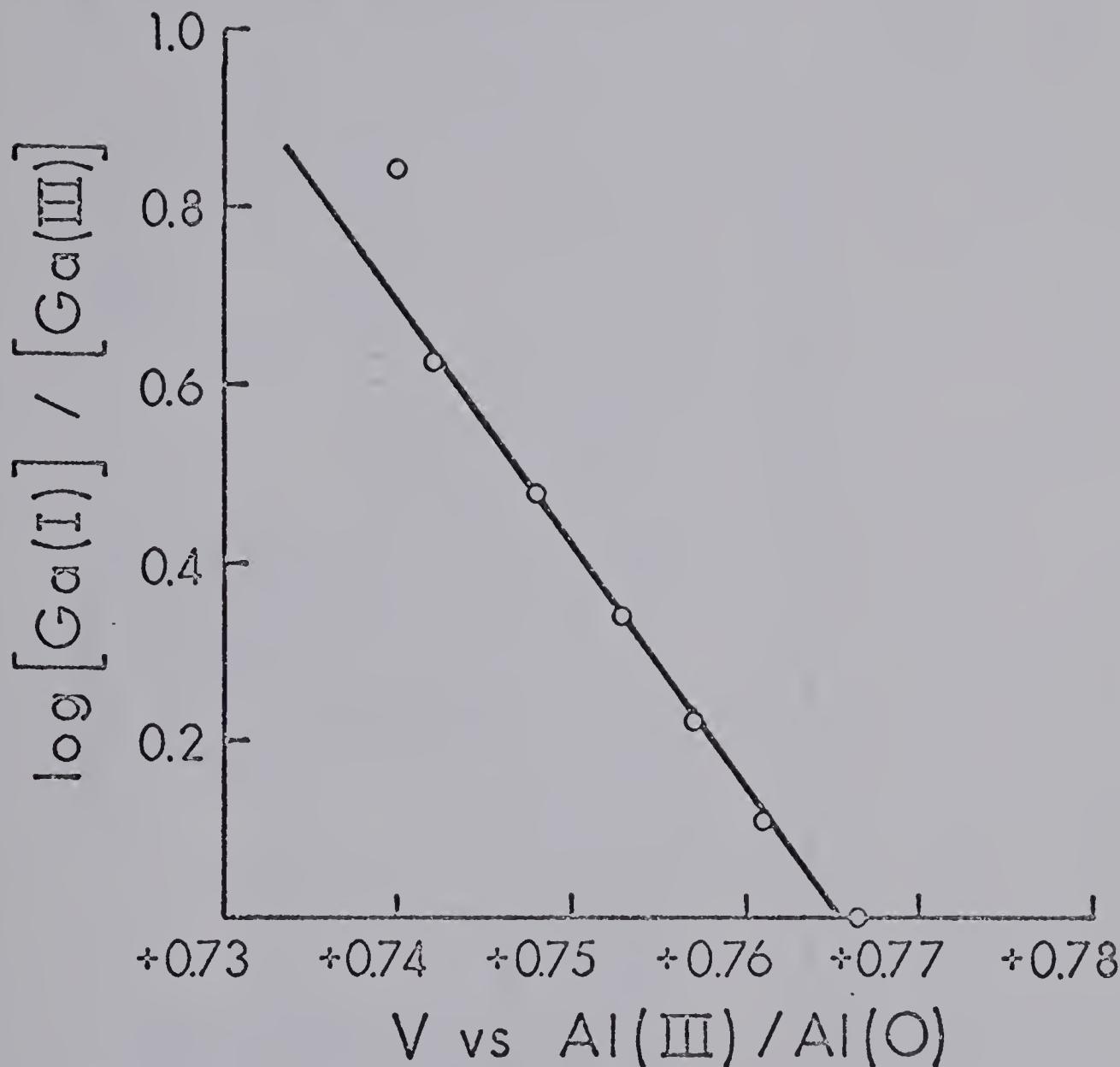


Figure 3. Nernst plot for the Ga(III)/Ga(I) couple.

Typical run, concentration on molal basis,  
obtained by coulometric reduction of  
Ga(III) at platinum electrode.



TABLE IIEquilibrium Constants for Group IB, IIB and IIIA Elements

<u>Equilibrium</u>	<u>AlCl<sub>3</sub>-NaCl-KCl</u>	<u>LiCl-KCl 450°C (a)</u>	<u>H<sub>2</sub>O, 25°C</u>
Cu(II) + Cu(O) ⇌ 2Cu(I)	2.1 × 10 <sup>14</sup>	7.1 × 10 <sup>6</sup>	5.9 × 10 <sup>-7</sup> c
Ag(II) + Ag(O) ⇌ 2Ag(I)	>3 × 10 <sup>12</sup>	>3 × 10 <sup>7</sup>	1 × 10 <sup>20</sup> c
1/2Au(III) + Au(O) ⇌ 3/2Au(I)	>2 × 10 <sup>-20</sup>	>4 × 10 <sup>-1</sup>	3.4 × 10 <sup>-2</sup> c
Zn(II) + Zn(O) ⇌ 2Zn(I)	very small	very small	very small
Cd(II) + Cd(O) ⇌ 2Cd(I)	2.6 × 10 <sup>1</sup>	3.6 × 10 <sup>4</sup>	very small
Hg(II) + Hg(O) ⇌ 2Hg(I)	3.6 × 10 <sup>4</sup>	-	1.6 × 10 <sup>2</sup> c
1/2Ga(III) + Ga(O) ⇌ 3/2Ga(I)	5.0 × 10 <sup>6</sup>	-	3.0 × 10 <sup>-10</sup> b
1/2In(III) + In(O) ⇌ 3/2In(I)	>4 × 10 <sup>13</sup>	-	1.9 × 10 <sup>-6</sup> b
1/2Tl(III) + Tl(O) ⇌ 3/2Tl(I)	>4 × 10 <sup>25</sup>	-	2.3 × 10 <sup>27</sup> b

(a) Ref. (34)

(b) Ref. (40)

(c) Ref. (43)

181 3  
444 3

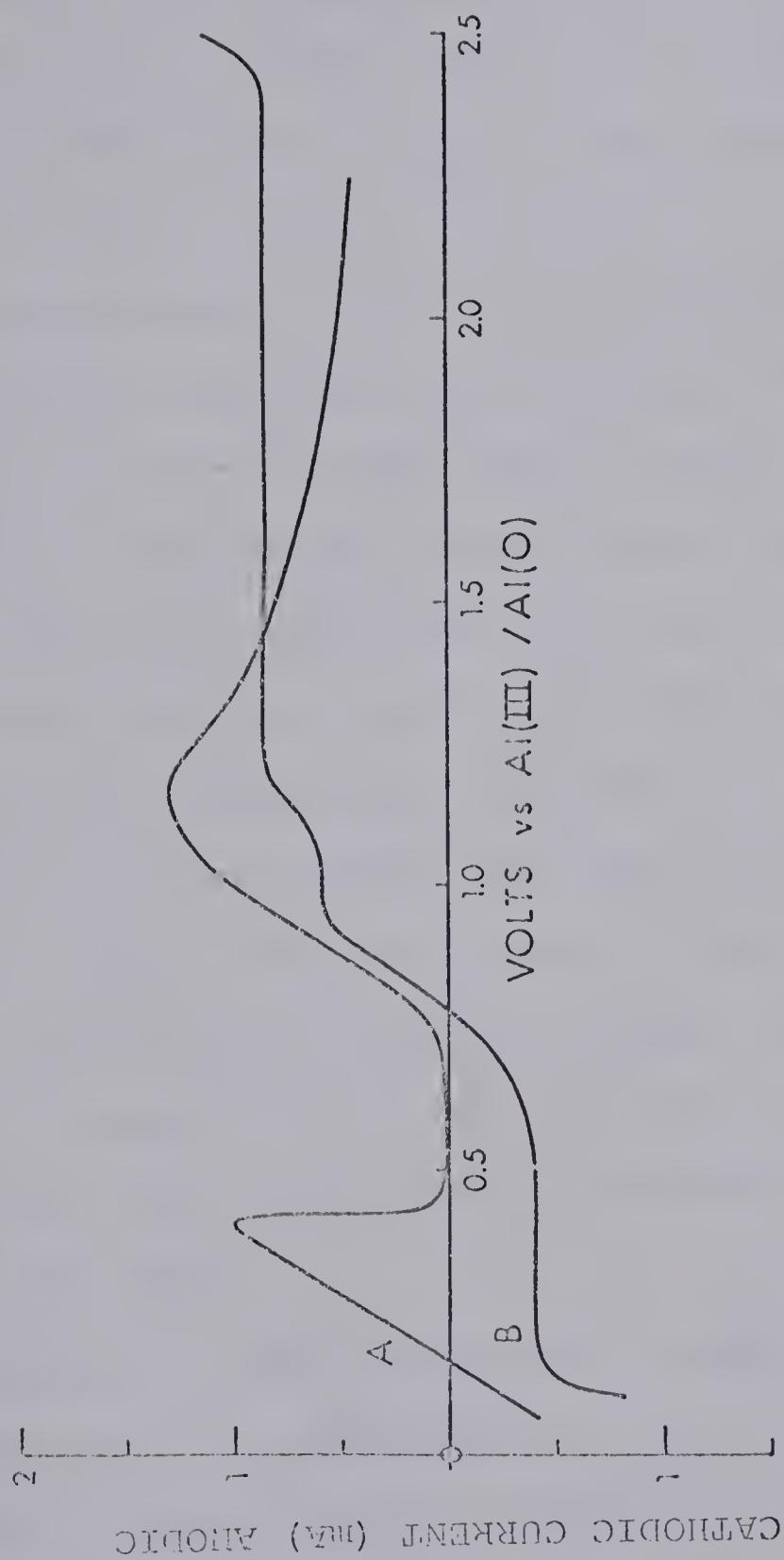


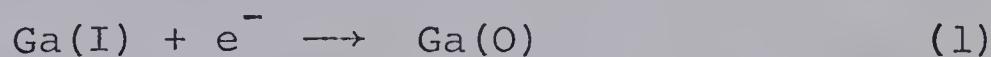
Figure 4. Voltammetry of gallium ions. A, 0.1 molal Ga(II), 0.04 v/sec; B, 0.05 molal Ga(II), 0.05 molal Ga(III), 0.02 v/sec. Tungsten microelectrodes, scan direction toward positive potential.



deposition of gallium metal at the tungsten electrode. The tungsten is covered rapidly with gallium and thereafter behaves like a gallium electrode. Curve A passes through the zero current axis at  $0.16 \pm 0.01$  V which is in good agreement with the equilibrium potential of the Ga(I)/Ga(O) couple,  $0.160 \pm 0.002$  V.

The deposited gallium metal is stripped off at potentials more oxidizing than this equilibrium value, giving rise to the observed anodic current. After the stripping is complete the current drops back to zero. The area under this anodic wave is equal to the area under the preceding cathodic wave because the amounts of gallium deposited and stripped off are equal. As shown by the coulometric oxidation mentioned above, Ga(I) is oxidizable to Ga(III); this oxidation begins at approximately 0.7 V on Curve A. This peak is slightly broader than those usually observed voltammetrically (39) but this is due primarily to the IR drop. As will be seen later Curve B shows waves rather than peaks.

Curve B of this figure shows a scan of a solution containing equal concentrations of Ga(I) and Ga(III). As with Curve A, gallium metal is deposited at the tungsten electrode:



In the presence of Ga(III), a favorable equilibrium constant (Table 2) exists for the chemical reaction of this



gallium metal:



However, at the same time Ga(III) is also reduced electrochemically:



In scanning towards more oxidizing potentials, reaction (1) will decrease and so will reaction (2). The retardation of (2) will make more and more Ga(III) available for reaction (3). The observed current will therefore drop rapidly in the neighbourhood of the Ga(I)/Ga(O) couple and then level off as reaction (3) takes over. Reaction (3) will continue until the Ga(III)/Ga(I) equilibrium potential at  $0.766 \pm 0.002$  V is reached. The voltammetric value obtained is  $0.77 \pm 0.02$  V.

At more oxidizing potentials, Ga(I) is oxidized to Ga(III) and thus gives rise to an anodic current as in Curve A. After correction for the IR drop in the cell (250 ohms, primarily in the frit of the compartment) it can be seen that the first wave of Curve B corresponds to the one in Curve A.

The first anodic wave in Curve B is followed by a second, suggesting further oxidation of Ga(III). However, a voltammetric scan of a solution of pure  $\text{GaCl}_3$  shows no such second anodic wave, and the cathodic wave observed on attempted reduction of Ga(III) to Ga(I) appears at the



expected potential. The shapes of the second anodic wave (Curve B) and the cathodic reduction wave are not simple; the significance of this is not clearly understood and may be due to slow kinetic steps in the oxidations and reductions involved.

### Indium

Indium metal in contact with the melt reacts with it completely to give aluminum metal. From the amount of indium metal put into the melt and, in the case of a complete reaction, of aluminum metal obtained, it is ascertained that In(I) was formed in solution by the reaction  $\text{Al(III)} + 3\text{In(0)} \rightarrow \text{Al(0)} + 3\text{In(I)}$ . The In(I)/In(0) couple must therefore be more negative in potential than the Al(III)/Al(0) couple. Inside the melt range In(I) can be oxidized; a voltammetric scan indicates oxidation at  $1.2 \pm 0.1$  V. Likewise, the addition of  $\text{InCl}_3$  and subsequent scanning results in a cathodic wave at  $1.1 \pm 0.1$  V. More precise potentiometric measurements could not be made because  $\text{InCl}_3$  scarcely dissolves into the melt even if the temperature is raised to  $220^\circ\text{C}$  while In(I) could not be quantitatively oxidized at higher In(I) concentrations. It is concluded that the waves seen in voltammetry correspond to the oxidation of In(I) to In(III) and reduction from In(III) to In(I).

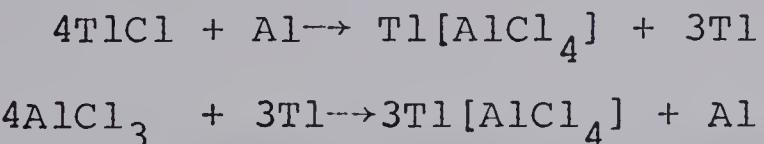
The data obtained allow estimation of K for the reaction  $1/2\text{In(III)} + \text{In(0)} \rightleftharpoons 3/2\text{In(I)}$ . The value obtained (Table 2) is  $> 4 \times 10^{13}$ .



### Thallium

Thallium metal also reacts with the melt with production of aluminum. It was shown, by the method described above for indium, that thallium exists as Tl(I) in the melt. It is, however, not possible to further oxidize Tl(I) to Tl(III) inside the melt range. The equilibrium constant K for the reaction  $1/2\text{Tl(III)} + \text{Tl(O)} \rightleftharpoons 3/2\text{Tl(I)}$  is then  $K > 4 \times 10^{25}$ , which is comparable to the aqueous value of  $K = 2.3 \times 10^{27}$  (40).

The chemistry of the thallium/aluminum system has been studied in detail by Palkin and Palyura (41). On the basis of the results of differential thermographic and quantitative chemical analysis the following ternary reciprocal displacement system was established:



The driving force of the above reactions, in the opinion of the Russian authors, arose from the formation of the highly stabilized compound  $\text{Tl}[\text{AlCl}_4]$ .

Although the authors used a completely different solvent system ( $\text{AlCl}_3$  under pressure) their findings agree with with this thesis. In this light Delimarskii's report (42) in which he quotes a value of 0.3 V for thallium in  $\text{NaAlCl}_4$  at 300°C seems to be doubtful. Unfortunately the way of measurement and definition of these potentials are not known since the original paper was not accessible. A further



uncertainty was his use of a platinum wire inserted into the melt as a reference electrode. The shortcomings of a reference electrode of this type have been discussed earlier in this thesis. It may also be pointed out that the other data (42) appear to be unreliable. This may be due in part to a misprint in the English abstract (42). Zinc and cadmium were reported in the text as having two waves while the table quotes two waves for cadmium and tin. Further,  $\text{BiCl}_3$  was reported as having only one potential (kind unspecified) while Yntema (15) had reported investigations on bismuth 10 years earlier where he mentioned the additional wave. Direct comparison of other work in this field with Delimarskii's must therefore be done with caution.

### Copper

Yntema (13) measured the decomposition potential of  $\text{Cu(I)}$  from which a value of  $E^\circ = 0.81 \pm 0.03$  V was calculated (14) on the mole fraction scale. He made no attempt to oxidize  $\text{Cu(I)}$  to  $\text{Cu(II)}$ . In the present study potentials of both the  $\text{Cu(I)}/\text{Cu(0)}$  and  $\text{Cu(II)}/\text{Cu(I)}$  couples were measured accurately which allowed the determination of their standard potentials and equilibrium constants. A value of  $0.710 \pm 0.002$  V was obtained for the molal standard potential of the  $\text{Cu(I)}/\text{Cu(0)}$  couple.  $\text{Cu(I)}$  was then oxidized coulometrically at inert electrodes in the same manner as  $\text{Ga(I)}$ .

Plotting the coulometric data as  $\log [\text{Cu(I)}]/[\text{Cu(II)}]$  vs.



e.m.f. resulted in a straight line with a slope corresponding to  $1.0 \pm 0.1$  electrons. The standard potential was measured at equal concentrations of Cu(I) and Cu(II) as  $1.866 \pm 0.001$  V. A voltammetric scan of a solution containing equal concentrations of Cu(I) and Cu(II) is shown in Fig. 5. The interpretation of these curves is similar to that of the curves in Fig. 4.

The solution of Cu(II) in this melt is green in color while the solution of Cu(I) is colorless. The equilibrium value for the reaction  $\text{Cu(II)} + \text{Cu(0)} \rightleftharpoons \text{Cu(I)}$ , with K defined using molal concentrations, is  $K = 2.1 \times 10^{14}$  which is much larger than the aqueous value of  $5.9 \times 10^{-7}$  (43); the equilibrium in acetonitrile, however, is favored by an even larger constant of  $2.5 \times 10^{25}$  (44).

### Silver

The Ag(I)/Ag(0) couple has been measured previously (2) at  $150^\circ\text{C}$  and a value of  $0.795 \pm 0.001$  V was reported. In the present study the molal standard potential obtained was  $0.719 \pm 0.001$  V at  $135^\circ\text{C}$  with a temperature dependence of  $-0.44 \pm 0.03$  mV/ $^\circ\text{C}$  from 120 to  $170^\circ\text{C}$  (Figure 6). The temperature vs. e.m.f. plot did not show any hysteresis. The slope of the Nernst plot of the anodization corresponded to  $1.0 \pm 0.1$  electrons. Figure 7, Curve A, shows the first seven points out of a total of ten which established the slope.

Anodizing silver in another experiment at  $150^\circ\text{C}$  resulted



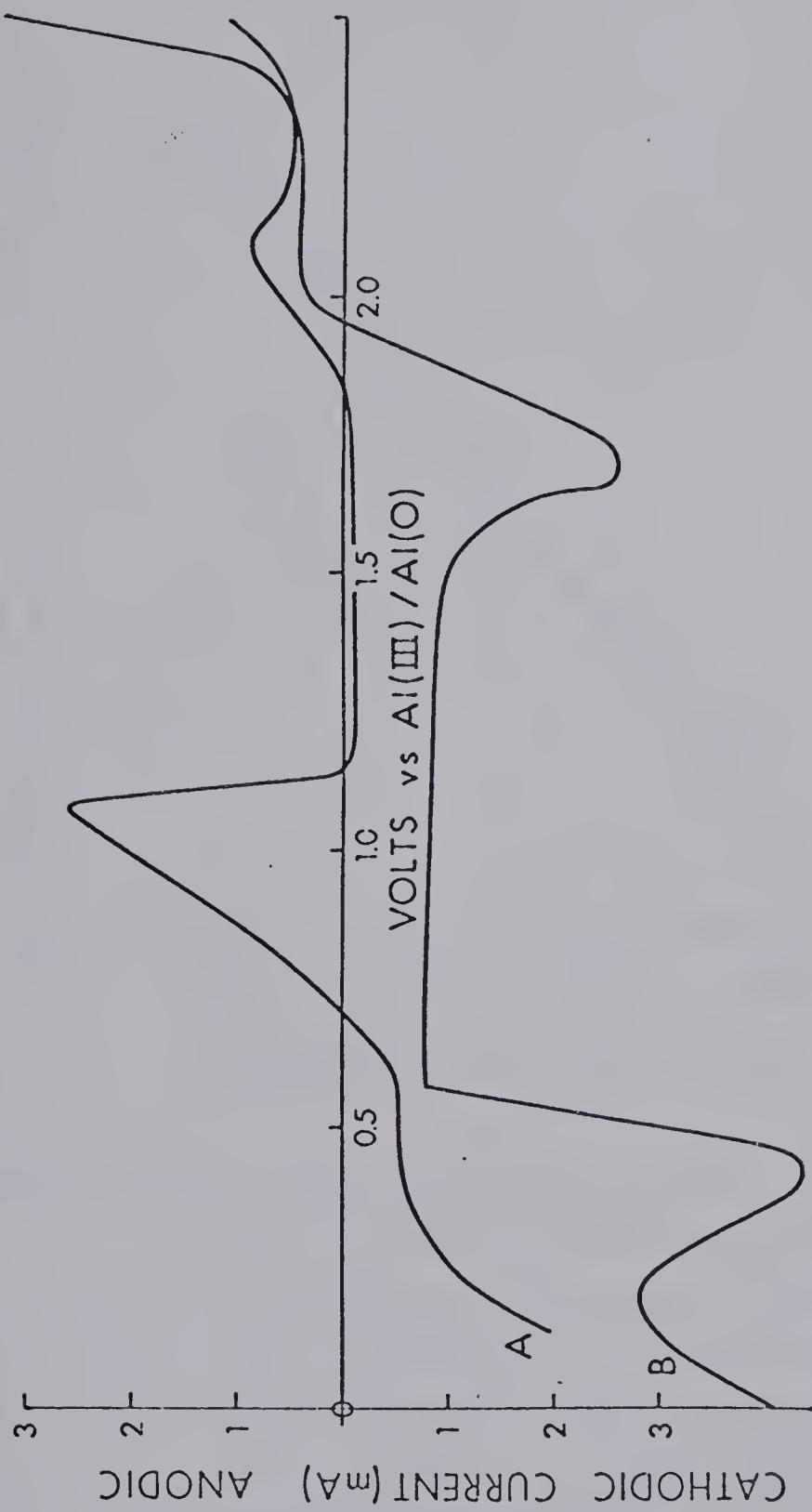


Figure 5. Voltammetry of a solution containing Cu(I) and Cu(II).  
Curve A scan in positive direction, Curve B scan in negative direction.



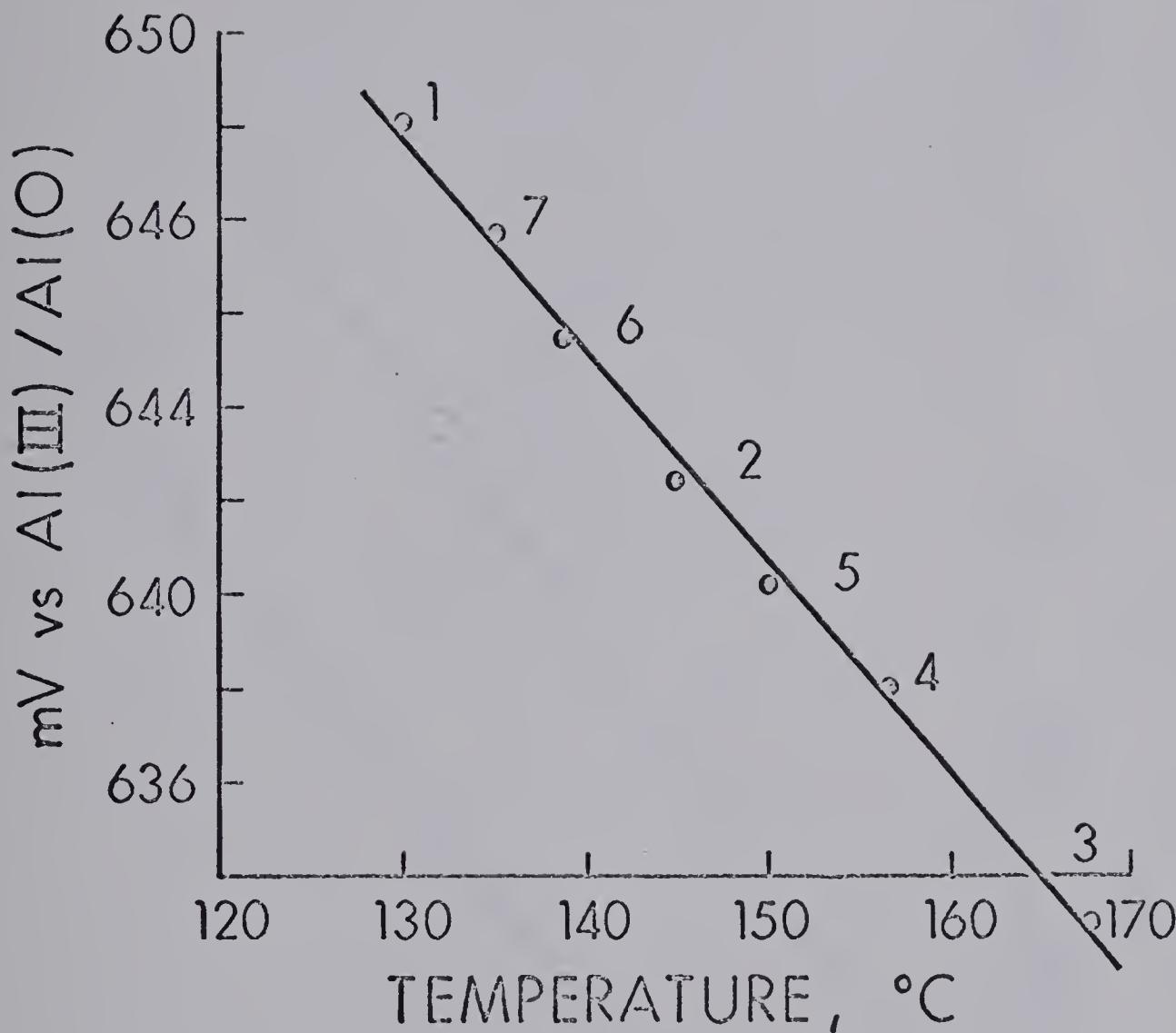
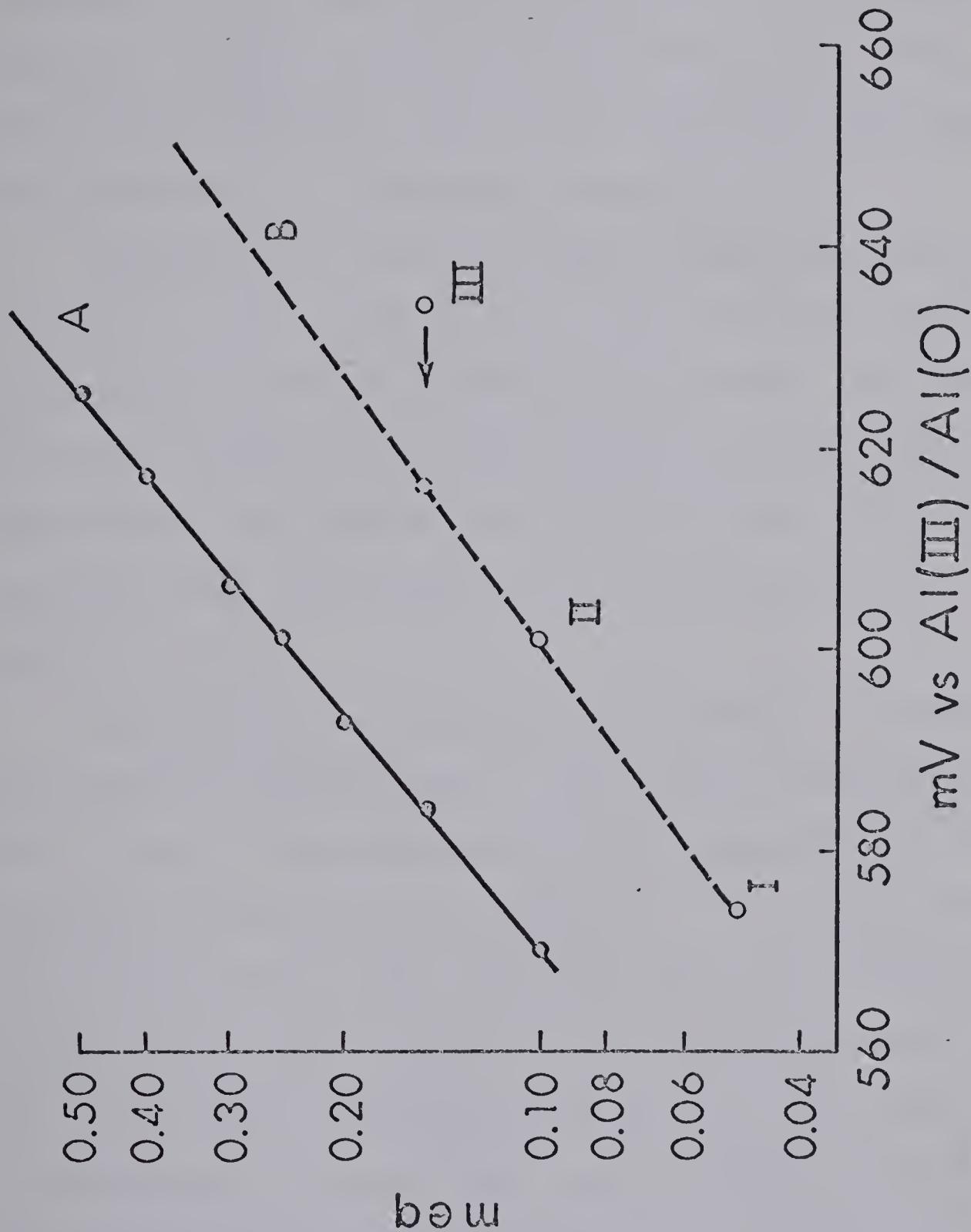


Figure 6. Temperature dependence of the Ag(I)/Ag(O) couple vs. Al(III)/Al(O) reference electrode. Numbers refer to succession of points measured. Ag(I) concentration approximately  $10^{-1}$  moles/kg. Same experiment as Figure 7, Curve A.





**Figure 7.** Nernst plot of  $\text{Ag}(\text{I})/\text{Ag}(\text{O})$  couple after coulometric anodization. Curve A, anodization current 10 mA; current density approximately  $11 \times 10^{-2} \text{ A/cm}^2$ . Curve B, anodization current 50 mA; current density approximately  $5.5 \times 10^{-2} \text{ A/cm}^2$ .



in a value of 0.729 V for the standard potential with  $n = 1.1$ . The experimental conditions such as concentration and current densities during anodization were identical to the ones of the previous runs at 135°C. However, weighing the silver wire before and after the experiment disclosed that more silver metal was lost than corresponded to the faradaic process.

Reducing the amount of melt inside the compartments as well as the current density (now  $5 \text{ mA/cm}^2$ , thus being comparable to (2)) in another run resulted in a molal standard potential of 0.736 V with  $n = 0.97$ . This value approached the reported value (2) of 0.795 V better than the previous ones but was still far from satisfactory agreement.

In Figure 7, Curve B, an anodization was performed at higher current density. The concentration of silver ion at point I was roughly  $7 \times 10^{-3}$  moles/kg, assuming a faradaic process with one electron. It can be seen in Figure 8, Curve I, that the potential stabilized inside a short time and remained stable. Using the data for point I a molal standard potential of 0.749 V can be calculated which is again far from the value of 0.795 V reported by Hames and Plambeck (2,3) but is in reasonable agreement with that of the previous experiment. A similar stability is observed for point II. The slope established by the two points (Figure 7, Curve B) is characteristic for  $n = 1$ .



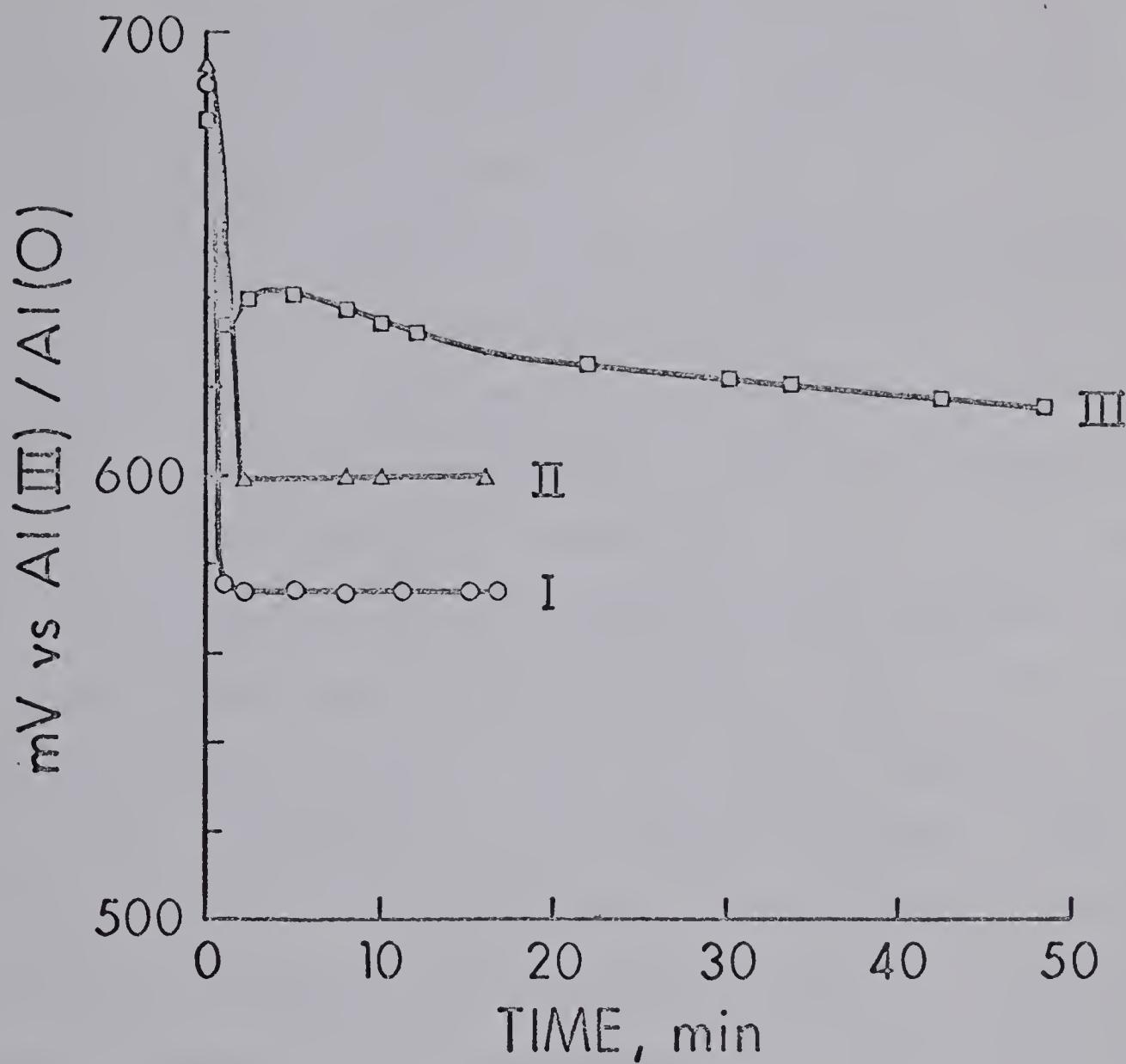


Figure 8. Time dependence of  $\text{Ag}(\text{I})/\text{Ag}(\text{O})$  vs.  $\text{Al}(\text{III})/\text{Al}(\text{O})$  reference electrode. Curves I, II, III refer to points I, II, III of Figure 7, Curve B.



Point III, however, is 20 mV from where it should be at the end of the anodization. It drifted slowly towards the line established by I and II which it reached after 45 minutes. The drift of the potential after 45 minutes had slowed down to 0.3 mV/min.

These data, especially those of Figure 8, show that the drift is not caused by combination of silver ions with melt impurities. At the lower concentrations of points I and II melt impurities would show a much more pronounced drifting than at higher concentrations. The reverse, however, is observed: there is no drift at low concentrations but a very strong initial drift at high concentrations. Also, the amount of silver lost was always significantly larger than corresponded to the faradaic process. The drifting of III in this light has to be explained as the production of polymeric silver species after the originally produced silver ion entity diffuses back to the electrode with which it will then react chemically. At low current densities and concentrations the polymeric species may be produced directly and stable potentials result.

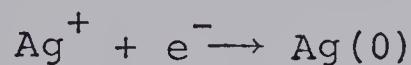
This, together with the consistent value of one electron and each anodization, seems to suggest a complex silver species in solution e.g.,  $\text{Ag}_q^{p+}$  with q and p depending on the experimental conditions.

In the case of bismuth,  $\text{Bi}^+$ ,  $\text{Bi}_4^{4+}$ ,  $\text{Bi}_5^{3+}$ ,  $\text{Bi}_8^{2+}$  have been conclusively shown to exist in chloroaluminate melts (6-12). Yntema added  $\text{Bi}_2\text{O}_3$  and observed one very



well-defined break in the current - voltage curve at low current densities. He noticed the production of a reddish brown compound at the cathode surface which could be isolated by immersion of the electrode in 95% ethanol. The substance decomposed in contact with water (17). This compound may well be identical with one of the low valence ions of bismuth mentioned before. It is reported (10) that  $\text{Bi}_5[\text{AlCl}_4]_3$  is of reddish color. Recently, Mamantov and coworkers (45) reported preliminary electrochemical investigations of the reduction of the Bi(III) ion by voltammetric methods. They observed three reduction waves, one including a two electron step.

It must be stated in conclusion that one cannot assume that the potential of the silver ion/silver couple corresponds to the simple reaction:



### Gold

Gold was anodized into solution at low current densities with a slope corresponding to  $1.1 \pm 0.1$  electrons. Several of the earlier anodization runs were unsuccessful in that no stable potentials could be obtained. Inspection of the gold wire after these experiments showed that anodization had occurred only in a few spots where it had resulted in the formation of deep pin holes. The holes showed the crystalline structure of the metal wire. It was found that remelting the wire before use tended to



prevent deep holes although dissolution was still not uniform. Stable potentials were thus obtained, however, and a molar standard potential of  $2.046 \pm 0.002$  V was calculated for the Au(I)/Au(0) couple. This value is much higher than those for Cu(I)/Cu(0), 0.710 V, and Ag(I)/Ag(0), 0.719 V. The solution containing Au(I) is orange in color while those of Cu(I) and Ag(I) are colorless.



### C O N C L U S I O N

It has now been shown electrochemically that low valence ionic species of group IB, IIB and IIIA exist in chloroaluminate melts. There are further indications that low valence states can be expected for many other elements such as bismuth and manganese. The species produced can be characterized by spectroscopic and/or electrochemical methods. It has been proven that the effects observed are not due to melt impurities.

The unambiguous characterization of low valence ions in the chloroaluminate melts makes a reconsideration of these and similar ions in other melts necessary. For example it appears from the published data that an unreported monovalent gallium species may well exist in the fused LiCl-KCl system.



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PART III

## STRUCTURAL MELT UNITS AND SOME RELATED PROBLEMS

IN THE AlCl<sub>3</sub>-NaCl-KCl EUTECTICA B S T R A C T

It is postulated that the ternary mixture composed of 66 mole % AlCl<sub>3</sub>, 20 mole % NaCl, and 14 mole % KCl gives rise to a Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> species in the molten and probably also in the solid state. Investigations by nuclear magnetic resonance of sodium-23, aluminum-27, and chlorine-35 nuclei as well as the available literature data suggest the formation of a large Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> anion while the cations are assumed to occupy the holes left by the bulky anions.

The equilibrium constant for the observed thermal decomposition of the Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> according to



was calculated as  $3 \times 10^{-4}$ .

The behavior of oxide ion in the molten ternary AlCl<sub>3</sub>-NaCl-KCl mixture is explained by the formation of anionic oxide-AlCl<sub>3</sub> complexes.

New evidence was found for the dissolution of a reducing aluminum species into the ternary melt.



I N T R O D U C T I O N

The observed low valence states of Group IB, IIB, and IIIA elements (1,2) as well as those of bismuth, tin, and lead (3-11) in chloroaluminate melts should be rationalized by, at least, a qualitative model. In order to do this, the physicochemical behavior of the melt and the entities comprising it must be understood. Most authors (3-14) have considered this system as consisting basically of  $\text{Na}[\text{AlCl}_4]$  with varying amounts of dissolved  $\text{AlCl}_3$ . Corbett (3-6) used a system composed of  $\text{Na}[\text{AlCl}_4]$  with 3 - 7 mole %  $\text{AlCl}_3$ .

It was realized that a characterization of the ternary system  $\text{AlCl}_3\text{-NaCl-KCl}$  could be done by its comparison with the similar systems  $\text{Na}[\text{AlCl}_4]$  and  $\text{AlCl}_3$  which have been investigated in detail in the past. Literature checks concerning the ternary mixture reveal that a surprising amount of unrelated information already exists. During the work of this thesis, the data were further augmented by NMR and X-ray measurements.

Solid  $\text{AlCl}_3$  is known to have an ionic layer structure (15). On melting its volume increases 83% (16) which is caused by the formation of the molecular species  $\text{Al}_2\text{Cl}_6$  (17). The structural units of this melt can be visualized as two distorted  $\text{AlCl}_4$  tetrahedra sharing one edge (17). The equivalent conductance of  $\text{AlCl}_3$  decreases at the melting point due to the formation of the molecular species and was determined as  $1.9 \times 10^{-5} \text{ cm}^2/\text{ohm equiv.}$  at  $200^\circ\text{C}$  (18).



The reaction of  $\text{AlCl}_3$  with an alkali metal chloride MCl in a 1:1 mole ratio results in the formation of  $\text{M}[\text{AlCl}_4]$  (19,20). The crystal structure of  $\text{Na}[\text{AlCl}_4]$  (21) shows a lattice made of nearly perfect tetrahedral  $\text{AlCl}_4^-$  ions with  $\text{Na}^+$  ions located in the empty spaces between the tetrahedra. The Al-Cl distance of  $2.13 \text{ \AA}$  is shorter than the sum of the tetrahedral covalent radii, while the Cl-Cl distance is  $3.48 \text{ \AA}$ . This was attributed to partial double bond character of the Al-Cl bond (21).

Sodium tetrachloroaluminate  $\text{Na}[\text{AlCl}_4]$  melts at  $151^\circ\text{C}$  (20) and a clear liquid may be obtained. Conductance measurements by Kryagova (22), Moss (23), and Midorikawa (24) point to the formation of  $\text{M}^+$  and  $\text{AlCl}_4^-$  entities in molten  $\text{M}[\text{AlCl}_4]$ . Raman investigations of molten  $\text{M}[\text{AlCl}_4]$  by Balasubrahmanyam and Nanis (25) and earlier by Gerdink and Houtgraaf (26) showed that  $\text{AlCl}_4^-$  is of tetrahedral symmetry. The Raman studies (25) established further the identity of spectra of liquid and solid  $\text{Na}[\text{AlCl}_4]$  and  $\text{K}[\text{AlCl}_4]$ . The absence of Raman lines other than those due to  $\text{AlCl}_4^-$  seemed to indicate purely electrostatic interactions between anions and cations. There can therefore be no doubt that  $\text{M}^+$  and  $\text{AlCl}_4^-$  are the typical structural units in alkali chloroaluminate melts within the time range of the spectral measurements i.e.,  $10^{-12} - 10^{-14} \text{ sec.}$

Reaction of  $\text{AlCl}_3$  with MCl in a 2:1 mole ratio above  $150^\circ\text{C}$  results in the formation of a liquid with eutectic



points between 100 and 200°C, depending upon M (19,20, 27-29). The ternary system  $\text{AlCl}_3\text{-NaCl-KCl}$  is of particular interest due to its low melting point of 98°C. The  $\text{AlCl}_3$ :  $(\text{Na},\text{K})\text{Cl}$  ratio is approximately 2:1 (27-29).

The ternary  $\text{AlCl}_3\text{-NaCl-KCl}$  system was first mentioned by Kendall, Crittenden and Miller (19) in 1923. The phase diagram of the same system was originally investigated by Wasilewski and coworkers (27) in 1935. These authors dwelt repeatedly on the tendency of the ternary system towards supercooling. Temperature vs. time plots of the cooling curves showed a large amount of supercooling with the loss of the subsequent plateau which had degenerated to a mere maximum (27). This effect may explain why the published data for the melting point of the eutectic are widely different among different authors. Although Wasilewski estimated the error to be 2-3°C (27) his melting point of 70°C could not be confirmed. Midorikawa (29), who also commented on the high degree of supercooling in detail, quotes 93°C as a melting point. By using a mechanical stirrer he claimed to have partially overcome the supercooling except in mixtures with a high KCl content. The composition for his eutectic was 60 mole %  $\text{AlCl}_3$ , 26 mole % NaCl and 14 mole % KCl. Although Treadwell's result (30) of 94°C agrees as far as the melting point is concerned, his composition was slightly different: 62 mole %  $\text{AlCl}_3$ , 26 mole % NaCl, and 12 mole % KCl.



Plotnikov (28) reported a melting point of 89°C for a composition of 63.5 mole % AlCl<sub>3</sub>, 20.0 mole % NaCl, and 16.5 mole % KCl. It appears from this that the supercooling, as well as the volatility of the AlCl<sub>3</sub> upon which most of the above authors also commented, will give rise to a difference of 5 to 10% in the composition.



E X P E R I M E N T A L

The purification of  $\text{AlCl}_3$  and the other chemicals used has been described in detail in Part II of this thesis.

NMR and X-ray samples were prepared by melting the components in a round bottomed flask inside the glove box. In the case of the NMR samples the liquid melt was transferred into the NMR tubes with disposable pipets. For the X-ray samples some melt was poured into a cold mortar which prevented formation of large crystals, finely ground with a mortar and pestle after cooling, and transferred into quartz capillaries. The NMR tubes were removed from the glove box after solidifying and sealed off under 10 mm Hg pressure. The capillaries were also closed outside the glove box without special precautions.

For  $\text{H}^1$ -NMR normal medium wall tubes were used while tubes of 10 mm O.D. were used for all wideline experiments.

The  $\text{H}^1$ -NMR was observed at 100 MHz and a 12 inch magnet (Varian Assoc.). The temperature was varied from 120 to 170°C. The nuclear magnetic resonances of  $\text{Na}^{23}$ ,  $\text{Al}^{27}$  and  $\text{Cl}^{35}$  were done at  $170 \pm 2^\circ\text{C}$ . A Model V-4200 B Wideline Spectrometer with a 12 inch magnet of approximately 14 Kg (Varian Assoc.) was used in conjunction with a Model 5100 B frequency synthesizer and Model 5110 B frequency synthesizer driver (Hewlett-Packard) which synchronized a Model V-4210A variable radiofrequency oscillator (Varian Assoc.). For audio frequency amplification a Parr JB-4



amplifier (Princeton Applied Research) was used which fed its output into a G-14 (Varian Assoc.) strip chart recorder.

A particular resonance frequency was found by first searching for it with the variable frequency oscillator. This frequency was then firmly synchronized by the frequency synthesizer through the use of a Model 140A oscilloscope (Hewlett-Packard).

The linewidths were recorded in the dispersion mode (31) and are given as peak-to-peak values. The linewidth calibration was performed with the frequency synthesizer in the following manner. With the magnetic field scanning one resonance was first recorded. The frequency was then altered on the frequency synthesizer and another resonance was recorded. The distance between the two resonances corresponded directly to the frequency change and was then used to measure the linewidth.

The X-ray powder patterns were obtained with molybdenum  $K_{\alpha}$  irradiation on a Philips PW 1009/80 X-ray generator. The lines were recorded on photographic film by a Monius camera.

Raman spectroscopy was done in a quartz cell 1 inch long and of 2 mm I.D. which was heated from the outside through a layer of resistance wire. A LR-1 (Perkin-Elmer) laser excited instrument was used.



R E S U L T S

In order to gain insight into the ion-solvent interaction, nuclear magnetic resonance studies were done using  $\text{Na}^{23}$ ,  $\text{Al}^{27}$ , and  $\text{Cl}^{35}$ .

Aluminum-27 possesses spin 5/2 and a quadrupole moment of 0.149; the resonance frequency at 10 Kg is 11.262 MHz. (32). The high quadrupole moment gives rise to line broadening which will decrease with increasing symmetry around the nucleus under consideration. Aluminum resonance has been used as early as 1957 (33-39) where  $\text{Al}(\text{III})$  was dissolved in aqueous as well as non-aqueous solvents. The value for aqueous  $\text{AlCl}_4^-$  was  $15.1 \pm 0.5$  Hz (37), while  $\text{AlI}_4^-$  was 42 Hz (37). This study reports a value of  $42 \pm 4$  Hz for a solution of  $\text{Al}(\text{NO}_3)_3$  in water at 27°C. The  $\text{Al}^{27}$  resonance of molten  $\text{Na}[\text{AlCl}_4]$  at 14 Kg and 15.67 MHz resulted in a linewidth of  $90 \pm 5$  Hz (Table I).

With  $(\text{Na},\text{K})[\text{Al}_2\text{Cl}_7]$  a linewidth of  $700 \pm 30$  Hz was obtained. Chemical shifts between this compound and  $\text{Na}[\text{AlCl}_4]$  could not be observed due to the broadness of the former line.

Sodium contains 100%  $\text{Na}^{23}$  with spin 3/2. Its magnetic moment is 2.22, the resonance frequency 11.262 MHz at 10 Kg. The quadrupole moment is again fairly high, 0.1 (32); a high symmetry environment is necessary to observe the resonance. So far,  $\text{Na}^{23}$  resonance has been studied only in water and



TABLE IRESULTS OF NMR MEASUREMENTS

Nucleus	Compound	Linewidth Hz
$\text{Al}^{27}$	$\text{Al}_2\text{Cl}_7^-$	700 + 30
	$\text{AlCl}_3:\text{NaCl}$	550 + 20
	1.4:1	
	$\text{AlCl}_4^-$	90 + 5
	$\text{Al}(\text{III}), \text{aq}$	42 + 4
$\text{Na}^{23}$	$\text{Al}_2\text{Cl}_7^-$	8.8 + 0.5
	$\text{AlCl}_4^-$	8.8 + 0.5
	$\text{NH}_4^+$ in $\text{Al}_2\text{Cl}_7^-$	54.1 + 0.2*
	$\text{NH}_4^+$ in $\text{AlCl}_4^-$	54.1 + 0.2*
$\text{Cl}^{35}$	$\text{Al}_2\text{Cl}_7^-$	7000 + 500
	$\text{AlCl}_4^-$	5000 + 500

\* N-H coupling



water-acetone solution (40,41). It has been observed that sodium must be highly ionic in order to obtain sharp resonance lines (42).

The linewidth of sodium in molten (Na,K) [Al<sub>2</sub>Cl<sub>7</sub>] measured at 15.87 MHz, was 8.8 ± 0.5 Hz (Table I). The reported value for aqueous solution is 11.5 Hz (40).

Samples containing NH<sub>4</sub><sup>+</sup> as a cation were prepared by replacing some of the NaCl in the ternary mixture by NH<sub>4</sub>Cl without otherwise changing the melt composition. Proton resonance of the NH<sub>4</sub><sup>+</sup> ion in (Na,K) [Al<sub>2</sub>Cl<sub>7</sub>] and Na[AlCl<sub>4</sub>] resulted in a well-defined triplet with an N-H coupling constant of 54.1 ± 0.2 Hz. The value for NH<sub>4</sub><sup>+</sup> in water at 25°C was measured as 53.5 ± 0.2 Hz (43).

Nuclear magnetic resonance of Cl<sup>35</sup> resulted in very broad lines. The linewidth in (Na,K) [Al<sub>2</sub>Cl<sub>7</sub>] was approximately 7000 Hz while Na[AlCl<sub>4</sub>] showed a linewidth of approximately 5000 Hz.

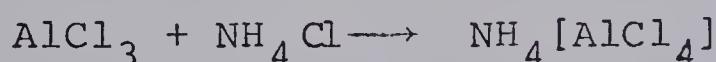
An attempt was also made to use Tl<sup>205</sup> nuclear magnetic resonance. The Tl<sup>205</sup> species with spin 1/2 has a magnetic moment of 1.61 (32,44) and resonates at 24.57 MHz at a field of 10 Kg. This nucleus was the first to be investigated in molten salt systems (45,46). More recent investigations show the sharp linewidth of Tl<sup>205</sup> even in solid samples (47).

The resonance frequency is higher than those available from the frequency synthesizer, and an attempt was made to use a 56.4 MHz oscillator with a corresponding increase in



field strength to 22.9 Kg. However, the experiments were not successful because of large inhomogeneities in the magnetic field which greatly reduced the sensitivity of the detection.

As part of the present study, the generation of an  $\text{Al}_2\text{Cl}_7^-$  species was demonstrated by electrochemical methods in addition to reported vapor pressure studies (48,49). Addition of  $\text{AlCl}_3$  to a compartment containing an Al(III)/Al(O) electrode in  $\text{Na}[\text{AlCl}_4]$  resulted in an increase in the electromotive force as measured versus an Al(III)/Al(O) reference electrode in  $\text{Na}[\text{AlCl}_4]$  (Figure 1). The positive sign of the emf is evidence for spontaneous formation of the  $\text{Al}_2\text{Cl}_7^-$  entity. Due to a large junction potential it is not possible to give an exact figure for  $\Delta G$ . It can however be estimated to be in the 10 - 20 Kcal/mole range. The curve peaks at a ratio of  $\text{AlCl}_3:\text{NaCl}$  of approximately 2:1 which corresponds to  $\text{Na}[\text{Al}_2\text{Cl}_7]$ . The  $\Delta G$  value is in agreement with the  $\Delta H$  value for the reaction



which was reported (50) as +13.3 Kcal/mole, if the  $T\Delta S$  term is small.



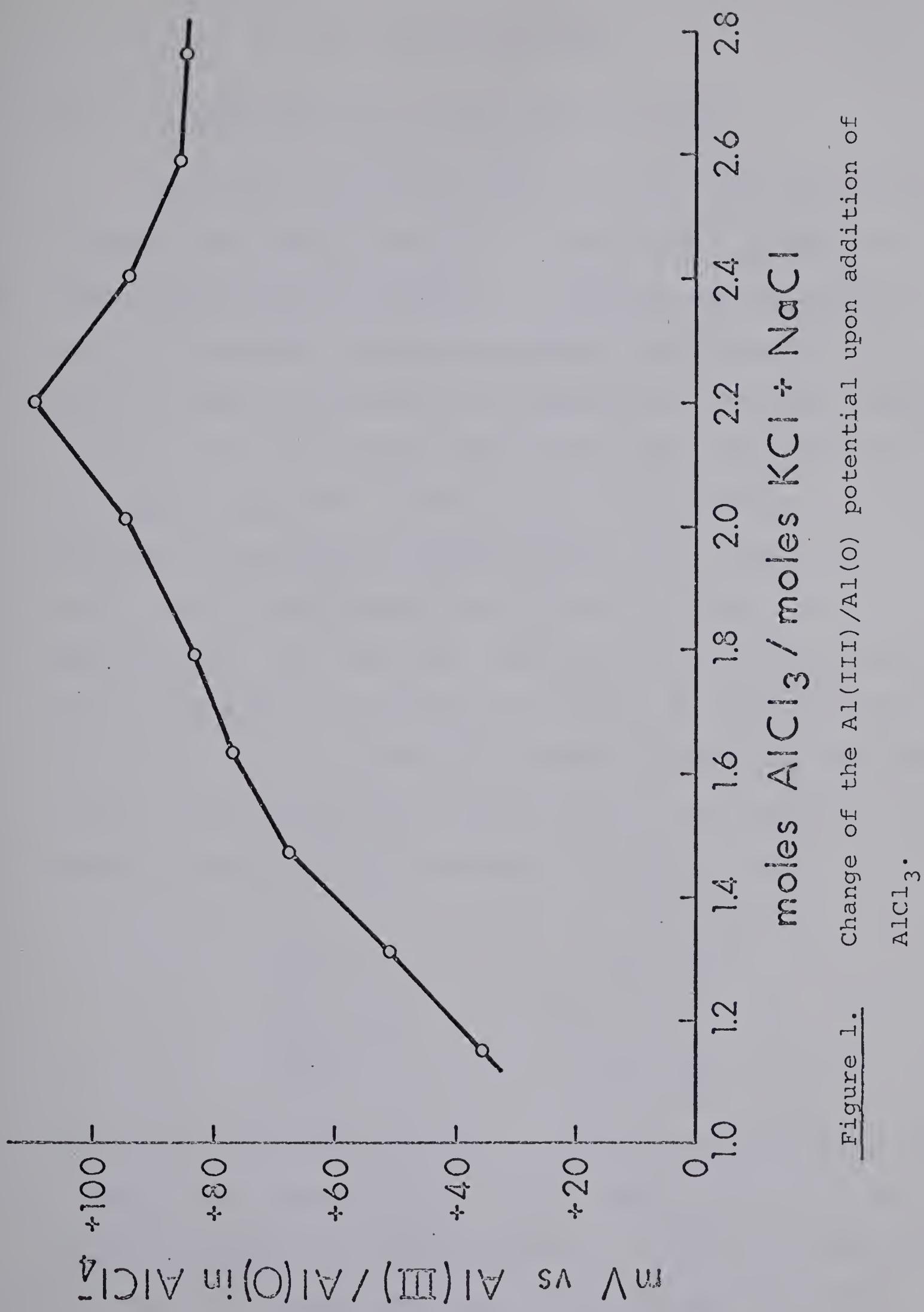


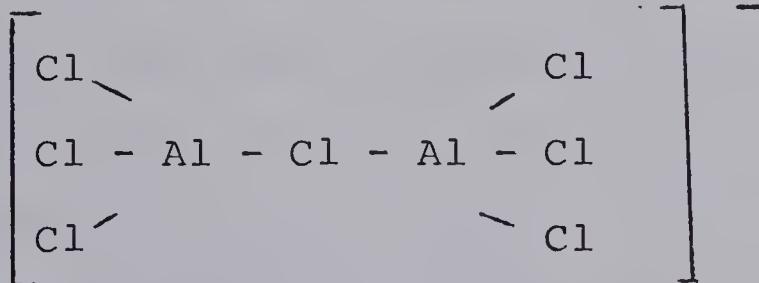
Figure 1. Change of the Al(III)/Al(O) potential upon addition of AlCl<sub>3</sub>.



## DISCUSSION

### (A) Structural Units in the Eutectic Melt.

A simple calculation shows that the  $\text{AlCl}_3\text{-NaCl-KCl}$  eutectic with 66:20:14 mole %, respectively, corresponds approximately to  $(\text{Na}, \text{K})[\text{Al}_2\text{Cl}_7]$ . Species corresponding to  $\text{Al}_2\text{Cl}_7^-$  have been recognized before. Complications in Friedel-Crafts alkylations and acylations have been traced to the formation of protonated arenes like  $[\text{ArH}_2^+] [\text{AlCl}_4^-]$  and  $[\text{ArH}_2^+] [\text{Al}_2\text{Cl}_7^-]$  (51) which are the main cause of the observed intense red to orange colors (52). Moore and Morrey (48,49) were the first to propose  $\text{Al}_2\text{Cl}_7^-$  in a melt system. The basis for this proposal was vapor pressure studies of  $\text{AlCl}_3$  over  $\text{AlCl}_3\text{-MCl}$  systems in the Al:M range from 1:1 to 2:1. However, no comments were made about the  $\text{Al}_2\text{Cl}_7^-$  species as such. Gruen (53) was the first to suggest the following structure for  $\text{Al}_2\text{Cl}_7^-$ :

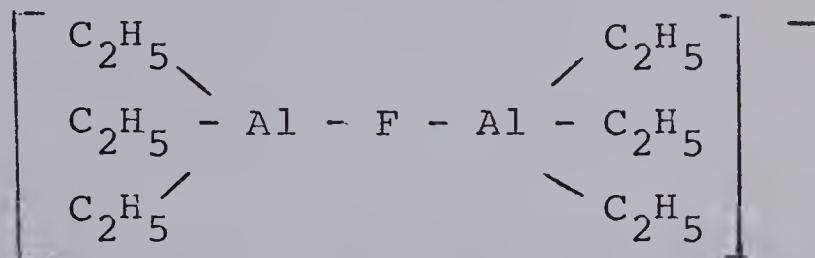


The only unambiguous proof of the above structure would come through Raman spectroscopy. In his paper Gruen (53) quoted work in progress at his laboratories in this direction but no later publication has appeared in the open literature. Raman spectroscopy by the author of this thesis did not give results



due to unremovable turbidity of the samples which caused too large an amount of scattering.

The only indication for the correctness of the above structure as proposed by Gruen (apparently unknown to him, although published somewhat earlier) comes from the field of organometallic aluminum chemistry. Ziegler (54) observed that  $\text{AlR}_3$  reacted with alkali halides MX to form complexes in 1:1 and 2:1 ratios. Subsequent X-ray analysis of  $\text{K}[\text{Al}_2(\text{C}_2\text{H}_5)_6\text{F}]$  by Natta and coworkers (55) resulted in the structure

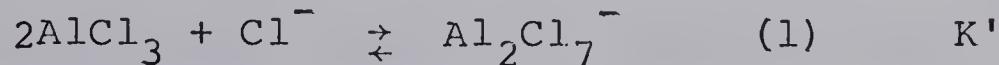


The main result, with respect to the present problem, was the establishment of tetrahedral symmetry around the aluminum atoms. Further information from the X-ray analysis of  $\text{K}[\text{Al}_2(\text{C}_2\text{H}_5)_6\text{F}]$  was an Al-F distance of  $1.80 \pm 0.06 \text{ \AA}$  which is close to that observed in  $\text{Na}_3[\text{AlF}_6]$  (56). The bonding in the organometallic aluminum anion was explained by the authors by assuming sp hybridization of the fluorine for the  $\sigma$ -bond, with partial  $\pi$ -bond character arising from overlap of the filled  $2p_y$  and  $2p_z$  orbitals of fluorine with the empty 3d orbitals of the aluminum. A similar type of structure and bonding mechanism can easily be visualized for  $\text{Al}_2\text{Cl}_7^-$ . One would expect the 3p - 3d overlap



to be weaker which would result in a weaker Al-Cl-Al bond. This has indeed been observed qualitatively: while  $K[Al_2(C_2H_5)_6F]$  can be dissolved in a weak base like ether, attempts to isolate  $Al_2Cl_7^-$  from the (Na,K)  $[Al_2Cl_7]$  eutectic in the same manner have so far failed (53).

The reaction of  $Cl^-$  with  $AlCl_3$  (13,48,49,53,57) results in the primary formation of  $Al_2Cl_7^-$ :



Further addition of  $Cl^-$  will result in the formation of  $AlCl_4^-$ :



The values of  $K'$  and  $K''$  at  $728^\circ C$  are approximately  $10^{13}$  and  $10^3$ , respectively (48,49). These data apply to systems with  $K^+$  as a cation. Smith (58) reported a value of  $10^5$  for  $K''$  at  $600^\circ C$  with  $Cs^+$  as the cation while Trémillon (13) gives  $10^6$  at  $175^\circ C$  with  $Na^+$  and  $K^+$  as cations. The differences in the equilibrium constants display the influence of the cations upon the anion as well as the temperature dependence of this interaction. Trémillon's value was chosen for the calculation of  $K'''$  since his system and temperature approached the ones used in the present system most closely.

Combining reactions (1) and (2) one obtains





Reaction (3) describes the observed physical decomposition of the  $\text{Al}_2\text{Cl}_7^-$  species.  $K'''$  can be calculated from  $K'$  and  $K''$  as approximately  $3 \times 10^{-4}$ . The tendency to break into  $\text{AlCl}_4^-$  and  $\text{AlCl}_3$  is therefore not very large, a fact which is displayed directly in the low vapor pressure of  $\text{AlCl}_3$  over these melts. At  $135^\circ\text{C}$  the vapor pressure is 11.5 mm Hg (30).

From the foregoing discussion it can therefore be assumed that the eutectic is composed mainly of  $(\text{Na},\text{K})[\text{Al}_2\text{Cl}_7]$ . It would be a contradiction, however, to state that the definitely observed eutectic corresponded to  $(\text{Na},\text{K})[\text{Al}_2\text{Cl}_7]$ . Compound formation always corresponds to a maximum in the phase diagram while a eutectic forms a minimum. Wasilewski (27) and Midorikawa (29) had, as was described earlier, great difficulties with the system, especially in the neighborhood of the eutectic point. Recently van Spronsen (59,60) published very careful investigations on mixtures of  $\text{AlBr}_3$  with KBr. He found the formation of a defined compound  $\text{K}[\text{Al}_2\text{Br}_7]$ , corresponding to a maximum in the phase diagram and a eutectic minimum of this compound with a 10 mole % increase of  $\text{AlBr}_3$  content. What can be suspected for the chloride system has thus been proven to exist for the bromide system. Early electrochemical investigations by Yntema (61-65) have shown that there appears to be no major differences in the solvation mechanism for other ions between the chloro- and bromoaluminate melts: the deposition potentials for most of



the investigated ions was nearly identical in the two solvents. This fact makes the extension of van Spronsen's results to the chlorides a reasonable one. It can therefore be assumed that the  $\text{AlCl}_3$ -NaCl-KCl system is a true eutectic, consisting mainly of  $(\text{Na}, \text{K})[\text{Al}_2\text{Cl}_7]$  with probably a small excess of  $\text{AlCl}_3$ . This would make the eutectic a binary one, and not a ternary one as quoted since Wasilewski. Macroscopic as well as microscopic evidence therefore points to  $\text{Al}_2\text{Cl}_7^-$  as the anionic melt entity.

Solid  $\text{Na}[\text{AlCl}_4]$  and  $(\text{Na}, \text{K})[\text{Al}_2\text{Cl}_7]$  showed different line patterns in the X-ray powder spectra.  $\text{Na}[\text{AlCl}_4]$  is known to exist in the solid lattice as  $\text{Na}^+$  and  $\text{AlCl}_4^-$  (21) and a possible break-up of  $\text{Al}_2\text{Cl}_7^-$  on freezing according to reaction (3) must be excluded since no lines corresponding to  $\text{AlCl}_4^-$  were seen. This suggests that a  $\text{Al}_2\text{Cl}_7^-$  anion is crystallizing as such without decomposition which is also demonstrated clearly by the maximum in the phase diagram in the case of the bromide system (59,60).

With the knowledge of the melt entities it is now possible to go one step further and examine the ion-solvent interaction. The linewidth studies with nuclear magnetic resonance which have been reported earlier in the result section were done with the hope of gaining insight into the symmetry environment of the different nuclei.

The tetracoordinated  $\text{AlCl}_4^-$  showed a linewidth of  $90 \pm 5$  Hz while a solution of aqueous Al(III) which is hexacoordinated (66) by water molecules showed a linewidth of



$42 \pm 4$  Hz. Unfortunately, a direct quantitative comparison between the two linewidths is not possible due to the different parameters which influence linewidth, such as temperature, viscosity, and susceptibility, in the two media.

Although it appeared at first that the broad line of  $(\text{Na}, \text{K})[\text{Al}_2\text{Cl}_7]$  indicated a drastic reduction of symmetry around the aluminum, later experiments showed that this is not the case. A sample composed of two separate tubes, one containing  $\text{Na}[\text{AlCl}_4]$  and the other  $(\text{Na}, \text{K})[\text{Al}_2\text{Cl}_7]$ , displayed both the narrow and the wide line. On the other hand, a sample with an  $\text{AlCl}_3:\text{NaCl}$  ratio of 1.4:1 in a single tube gave only a comparatively small reduction in linewidth to  $550 \pm 20$  Hz. It did not show two lines which would have corresponded to  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  and the broadening is interpreted as exchange corresponding to reaction (3).

The three measured linewidths for the chloroaluminates (Table I) allow a reevaluation of  $K'''$ . The observed linewidth  $\Delta\nu_{\text{obs}}$  of the mixture  $\text{AlCl}_3:\text{NaCl} = 1.4:1$  is related to those of  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  by (36, 67):

$$\Delta\nu_{\text{obs}} = P_{\text{Al}} \Delta\nu_{\text{AlCl}_4^-} + P_{\text{Al}_2} \Delta\nu_{\text{Al}_2\text{Cl}_7^-}$$

where  $\Delta\nu_{\text{AlCl}_4^-}$  and  $\Delta\nu_{\text{Al}_2\text{Cl}_7^-}$  are the linewidths of  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$ , respectively, while  $P_{\text{Al}}$  and  $P_{\text{Al}_2}$  are mole fractions, defined as usual by

$$P_{\text{Al}} = \frac{[\text{Al}]_{\text{AlCl}_4^-}}{[\text{Al}]_t}$$

$$P_{\text{Al}_2} = \frac{[\text{Al}]_{\text{Al}_2\text{Cl}_7^-}}{[\text{Al}]_t}$$



The total aluminum concentration  $[Al]_t$ , according to reaction (3), is given by

$$[Al]_t = [Al]_{AlCl_4^-} + [Al]_{Al_2Cl_7^-} + [Al]_{AlCl_3}$$

The last term in the last equation is considered to be small and will be neglected in the first approximation.

Using the numerical values of  $\Delta\nu_{obs} = 550$  Hz,  $\Delta\nu_{AlCl_4^-} = 90$  Hz,  $\Delta\nu_{Al_2Cl_7^-} = 700$  Hz,  $[Al]_t = 7.3$  molal (in the 1.4:1 mixture) one can solve the two simultaneous equations and obtains  $[Al]_{AlCl_4^-} = 1.8$  molal which corresponds to a  $AlCl_4^-$  concentration of  $[AlCl_4^-] = 1.8$  molal, and  $[Al]_{Al_2Cl_7^-} = 5.5$  molal or  $[Al_2Cl_7^-] = 2.8$  molal.

Since equilibrium constant for reaction (3) is given by

$$K''' = \frac{[AlCl_4^-][AlCl_3]}{[Al_2Cl_7^-]}$$

a numerical value is needed for the concentration of the  $AlCl_3$ . It can be obtained through the following relation:

$$\begin{aligned} [Cl^-]_t &= [Cl^-]_{AlCl_4^-} + [Cl^-]_{Al_2Cl_7^-} + [Cl^-]_{AlCl_3} = \\ &= 4 [AlCl_4^-] + 7 [Al_2Cl_7^-] + 3 [AlCl_3]. \end{aligned}$$

Insertion of  $[Cl]_t = 27.1$  molal,  $[Cl^-]_{AlCl_4^-} = 7.2$  molal,  $[Cl^-]_{Al_2Cl_7^-} = 19.6$  molal yields an  $AlCl_3$  concentration of 0.1 molal. From this one obtains  $K''' = 6.2 \times 10^{-2}$ . The discrepancy of this value with the one of  $3 \times 10^{-4}$  calculated earlier can be due to a variety of effects. The thermodynamic value for  $K'$  used in the previous calculation of



$K'''$  was measured at 728°C. At lower temperatures  $K'$  would be expected to decrease which would result in an increase of  $K'''$ . The temperature dependence of  $K'$  has not been reported. Furthermore, the value for  $K'$  was difficult to obtain experimentally (48,49) and must be considered as approximate only. On the other hand, several assumptions had also to be made in the calculation of  $K'''$  from the linewidth: equality of concentration and activity, negligible amounts of  $\text{AlCl}_3$  present, and no formation of chloroaluminate polymers.

It is felt that the value of  $K''' = 6.2 \times 10^{-2}$ , calculated from NMR measurements is somewhat too large due to the use of concentration instead of activity while the thermodynamic one is too low because  $K'$  was measured at 728°C. The present calculations therefore indicate  $10^{-4} < K''' < 10^{-2}$ .

Further evidence for the exchange according to (3) comes from another observation. The addition of one mole of  $\text{AlBr}_3$  to one mole  $(\text{Na},\text{K})[\text{AlCl}_4]$  will produce  $\text{Al}_2\text{Br}_3\text{Cl}_4^-$ . The aluminum halide subliming out of the melt under equilibrium conditions is pure  $\text{AlCl}_3$ ; only a fast nitrogen purging will liberate some bromide. The addition of  $\text{AlBr}_3$  and the subsequent sublimation of  $\text{AlCl}_3$  show at least a halogen exchange and most likely also point to a complete  $(\text{AlX}_3)$  - exchange.



The  $\text{Cl}^{35}$  nuclear magnetic resonance of  $\text{Na}[\text{AlCl}_4]$  and  $(\text{Na}, \text{K})[\text{Al}_2\text{Cl}_7]$  yield linewidths of 5000 and 7000 Hz, respectively (Table I). Their interpretation can be put on a semi-quantitative basis.

The relation governing the nuclear quadrupole relaxation in liquids (36, 67-70) is

$$\frac{1}{T_2} = \frac{3\pi^2}{10} \frac{2I+3}{I^2(2I-1)} \left(1 - \frac{\epsilon}{3}\right) \left(\frac{eQ}{h} \frac{\delta^2 V}{\delta z^2}\right)^2 \tau_c$$

where  $1/T_2 = \pi\Delta\nu$  with  $\Delta\nu$  being the peak to peak linewidth of the derivative in Hz,  $I$  is the spin of the nucleus under consideration,  $\epsilon$  is the assymmetry factor ( $0 < \epsilon < 1$ ),  $e$  is the electric charge,  $Q$  is the electric quadrupole moment,  $h$  is Planck's constant and  $\delta^2 V/\delta z^2$  is the gradient of the electric field at the nucleus.  $\tau_c$  is given by Debye's formula

$$\tau_c = \frac{4\pi\eta a^3}{3kT}$$

where  $a$  is the effective molecular radius,  $\eta$  is the viscosity,  $k$  is Boltzmann's constant and  $T$  is the absolute temperature.

$\tau_c$  is known as the correlation time and can be visualized as being the order of the time a molecule takes to turn through a radian or to move over a distance comparable with its dimensions (69). The term  $\frac{eQ}{h} \frac{\delta^2 V}{\delta z^2}$ , known as the quadrupole coupling constant, can be obtained directly from nuclear quadrupole resonance (71,72). The quadrupole coupling constant for  $\text{Cl}^{35}$  in  $\text{Na}[\text{AlCl}_4]$  was -22.6 MHz. This information together with the linewidth, allows the calculation



of the correlation time, if  $\epsilon$  is set equal to zero in the first approximation (73). Using  $\Delta\nu = 5000$  Hz one obtains  $\tau_c = 3 \times 10^{-10}$  sec, as compared to  $10^{-12} < \tau_c < 10^{-11}$  for water (69). The correlation time for  $\text{Al}_2\text{Cl}_7^-$  can be calculated as  $\tau_c = 4.2 \times 10^{-10}$  sec. The longer correlation time for  $\text{Al}_2\text{Cl}_7^-$  as compared to  $\text{AlCl}_4^-$  is most likely indicative for the larger size of the molecule as displayed by a in Debye's formula, assuming negligible change in the viscosity.

As mentioned earlier,  $\tau_c$  is characteristic for the whole molecule as such. This allows in turn the calculation of the quadrupole coupling constant of the  $\text{Al}^{27}$  nucleus in  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$ . For  $\text{AlCl}_4^-$  one obtains 1.7 MHz while the value obtained for  $\text{Al}_2\text{Cl}_7^-$  is 8.4 MHz. Reported values are 470 MHz for solid  $\text{AlCl}_3$  (74) and approximately 10 MHz for a solution containing the  $\text{Al}(\text{C}_2\text{H}_5)_3$  dimer (36) which is known to be in a rapid exchange equilibrium with its monomer. This equilibrium is therefore similar to that of the bridged  $\text{Al}_2\text{Cl}_7^-$  species. Due to the higher covalency in the organometallic aluminum species a somewhat larger coupling constant is encountered there. The coupling constant for solid  $\text{AlCl}_3$  was found to be representative for a bond which was 2/3 ionic and 1/3 covalent (74) which gave the aluminum a charge of +2. In the light of this interpretation the higher coupling constant in



$\text{AlCl}_4^-$  would mean an increase in the covalency of the Al-Cl bond and further lowering of the charge on the aluminum. This is in agreement with the general concept of coordination chemistry.

With regard to the cations one noticed immediately the extremely sharp line of the  $\text{Na}^{23}$  resonance of  $8.8 \pm 0.5$  Hz (Table I). No chemical shift was observed between the sodium resonance in  $\text{Na}[\text{AlCl}_4]$  and  $(\text{Na},\text{K})[\text{Al}_2\text{Cl}_7]$ . The sharpness of the sodium line in the two melts is attributed to a high symmetry around the sodium ion with, at the same time, a very weak interaction with the surrounding chloride ions. This agrees with what has been found for the  $\text{Na}[\text{AlCl}_4]$  by Raman spectroscopy (25,26) and shows again the similarity between the  $\text{Na}[\text{AlCl}_4]$  and  $(\text{Na},\text{K})[\text{Al}_2\text{Cl}_7]$  melts.

Nuclear magnetic resonance of  $\text{H}^1$  in  $\text{NH}_4^+$  showed an N-H coupling of  $54.1 \pm 0.2$  Hz (Table I) which was close to that observed in aqueous solution (43). One interpretation of this result is that the N-H angles remain the same in both solvents. This is, however, not too surprising because of the fairly rigid structure of the  $\text{NH}_4^+$  molecule. The N-H coupling must therefore be regarded as a much cruder measure of the environment of the cation than is the line-width in the case of sodium.

Gruen, as mentioned already, has proposed a solvation model where the ion, in his case a transition metal ion, is surrounded by two  $\text{Al}_2\text{Cl}_7^-$  anions and where 3 terminal chlorides of each anion give rise to an octahedral coordination



(53). This applied for liquid  $\text{Al}_2\text{Cl}_6$  as a medium. Looking at the  $\text{Na}^{23}$  resonance in the ternary molten mixture a similar interpretation seems plausible. The sodium is likewise surrounded octahedrally by the chloride atoms of two  $\text{Al}_2\text{Cl}_7^-$  molecules. The Al-Cl bond is much more covalent than the Na-Cl bond and the interaction of the sodium with the chloride atoms must be purely electrostatic. In other words, the sodium ion is in an extremely ionic state. Other cations will remain similarly isolated in the holes left by the bulky  $\text{Al}_2\text{Cl}_7^-$  anions. This, by the way, explains why all eutectics containing  $\text{Al}_2\text{Cl}_7^-$ , but with different cations, melt in the fairly close range from 100 - 200°C.

A deeper understanding into the behavior of cations other than the alkalis may be obtained through a discussion of the probable solvation process. This may be illustrated by a specific example. The Fe(III) ion is not stable in any medium as an ion of charge +3. It will interact with its coordinating molecules, e.g., chloride ions, and lower its high positive charge by the attraction of electron density to somewhere in the range of +0.4 (75). If, on the other hand, the Fe(III) ion is surrounded by  $\text{Al}_2\text{Cl}_7^-$  anions, the available electron density on a chloride is reduced since part of the electron density will be drawn towards the aluminum ion as well.

The Fe(II) ion, however, will need less stabilization from coordination in a pure chloride medium (e.g. LiCl-KCl) as well as in the  $\text{Al}_2\text{Cl}_7^-$  medium. This is due to its lower formal positive charge.



Therefore, Fe(III) is destabilized with respect to Fe(II) in the chloroaluminate melts. This statement is equivalent to that saying Fe(II) is stabilized with respect to Fe(III). The formation of Fe(II) is therefore thermodynamically more favored in the chloroaluminate system. Although the above example has not been investigated during the work of this thesis there is definite evidence for this in the equilibrium constants, Part II, Table 2. The lower oxidation state is always more favored in chloroaluminates.

Another way of lowering the stabilization needs (solvation energy) of an ion would be the reaction with a neutral metal atom, e.g., the electrode. This has been observed for silver, tin, lead and bismuth (3-11). Part II of this thesis concluded that Ag(I) reacts with the silver metal of the electrode to form species of the type  $\text{Ag}_q^{\text{P}+}$ . An extreme example would be a species like  $\text{Ag}_2^+$  where the positive charge is now spread out over two silver atoms. Since the charge is no longer an integer Smith (58) has coined the term "fractional charge" where no implication is made as to the actual number of atoms in a cluster. A typical and well characterized entity in this class is  $\text{Bi}_5^{3+}$  which can readily be prepared in form of the compound  $\text{Bi}_5[\text{AlCl}_4]_3$  (5).

Hames and Plambeck (1,2) and Corbett (6) have shown that Cd(I) is much more stable than Cd(II) in chloroaluminates. This agrees with the expected destabilization of



Cd(II) with respect to Cd(I). The dimerization of Cd(I) to  $\text{Cd}_2^{2+}$  (6) need not be explained on the basis of ion-solvent interaction. The  $d^{10} s^1$  state of the univalent ions of this group is apparently unstable and dimerization going to  $d^{10} s^2$  occurs through the formation of metal-metal bonds.

It was observed during the electrochemical work (Part II) that at low concentrations ( $10^{-3}$  molal) the Nernst plot showed deviations from the expected straight line. It could be argued that there is a different amount of catenation at low concentrations than at high ones. From  $10^{-2}$  to  $10^{-1}$  molal no deviations were observed which in this light would indicate formation of a cluster of constant fractional charge.

#### (B) The Oxide Ion.

The  $\text{O}_2/\text{O}^{2-}$  electrode could not be realized in this study in the  $(\text{Na}, \text{K})[\text{Al}_2\text{Cl}_7]$  melt despite several attempts with tungsten and platinum as electrode materials. The addition of oxide ion did not produce the expected Nernstian behavior either. Similarly, the addition of small amounts of  $\text{Li}_2\text{O}$  did not give rise to changes beyond a few millivolts in the case of the  $\text{Al}(\text{III})/\text{Al(O)}$  and  $\text{Ag}(\text{I})/\text{Ag(O)}$  couples. It appeared as if oxide ions disappeared in the melt.

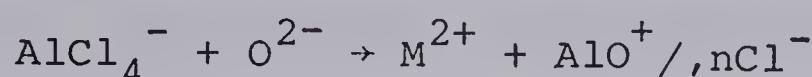
It has been argued earlier that the formation of  $\text{Al}_2\text{Cl}_7^-$  is due to the high Lewis acidity of  $\text{AlCl}_4^-$ . The



high basicity of  $O^{2-}$  will cleave  $Al_2Cl_7^-$  by acting upon the equilibrium of (3), thus resulting in the formation of  $AlCl_4^-$  and  $AlCl_3$ -oxide complexes. However, no confirmation of such a species was attempted.

Some interesting facts regarding the oxide ion problem arise from the comparison of Yntema's work on gallium (65) with this thesis. Yntema added gallium as  $Ga_2O_3$  to the melt. His results agree with the ones of this thesis where gallium ions were produced by coulometric oxidation of gallium metal. It must be assumed that the Ga-O bond was destroyed and Ga(III) produced. This case is not an isolated one. Yntema observed that  $K_2WO_6$  and  $WO_3$  gave the same deposition curve (65). Recent investigations of Russian workers (76) showed a eutectic of the system  $AlCl_3$ - $WOCl_4$  in a 3:1 mole ratio. Although this result can at the present time not be rationalized in terms of a compound there seems to be no doubt that the formation of Al-O containing species occurs.

A similar oxide-dissolving mechanism was proposed by Fremont and coworkers (12) for their system containing 60 mole %  $AlCl_3$ , 26 mole %  $NaCl$ , and 14 mole %  $KCl$ :



It may be noticed, however, that the authors did not recognize  $Al_2Cl_7^-$  as the anionic melt species. The reaction as written may be of some merit in melts containing  $AlCl_4^-$ .



Trémillon proposed in a recent paper (14) the formation of  $\text{AlOCl}$  and/or  $\text{Al}_2\text{OCl}_5^-$  in the  $\text{Na}[\text{AlCl}_4]$  system through the following reactions



and



The  $\text{Al}_2\text{OCl}_5^-$  is presumed to have the  $\text{Al}_2\text{Cl}_6$  structure.

(C) The Problem of Dissolved or Low Valence Aluminum in the Molten (Na,K)  $[\text{Al}_2\text{Cl}_7]$  System.

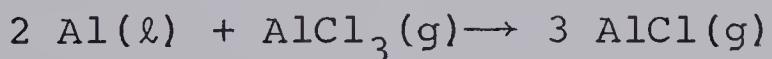
Hames and Plambeck (1,2) have shown that the  $\text{Al(III)}/\text{Al(O)}$  couple is essentially nonpolarizable in the  $\text{AlCl}_3 - \text{NaCl-KCl}$  eutectic. Earlier investigators (77,78) came to the same conclusion when trying to establish Tafel plots for the  $\text{Al(III)}/\text{Al(O)}$  electrode in molten salts. Hames (1) explained this on the basis of the high (approximately 6 molal) concentration of  $\text{Al(III)}$  in the melt.

On the other hand considerable evidence exists that some complications do arise. There can be little doubt that aluminum either dissolves into the melt as an uncharged species or it reacts with the melt with the formation of  $\text{Al(I)}$ . For instance, it was observed that when a  $\text{Au(I)}$  solution in a compartment with a C-porosity frit was placed inside the melt over aluminum metal, gold was precipitated within the glass frit. The two diffusing



species (gold and aluminum) presumably met inside the frit where the redox reaction then took place. Similar observations were made when the compartment contained Cu(I) ions. Smith (58) has observed dark coloration when aluminum metal was in contact with molten  $\text{Al}_2\text{Cl}_6$ . Munday (3) discussed in detail the formation of low valence aluminum species in the melt although he lacked chemical evidence. When aluminum metal was in contact with (Na,K)  $[\text{Al}_2\text{Cl}_7]$  a dark substance was observed to sublime out of the melt and condense at the cooler parts of the cell.

The existence of  $\text{AlCl}$  and  $\text{AlF}$  is well established in the vapor phase (79-81).  $\text{AlCl}$  can be prepared by the reaction



at temperatures above  $700^\circ\text{C}$  (73). The equilibrium constant lies at approximately  $10^{-9} \text{ atm}^2$  at  $900^\circ\text{C}$ . The  $\Delta H_f^\circ,_{298}$  was found to be  $-13.3 \pm 0.4 \text{ kcal/mole}$ . If it is attempted to extrapolate the temperature dependence of the equilibrium constant to  $200^\circ\text{C}$ , a value of approximately  $10^{-28}$  is obtained. Clearly, another mechanism, most likely solvation, must be assumed if  $\text{Al(I)}$  is to be considered as the produced entity.

Although this thesis cites direct evidence for a reducing aluminum species in solution, no quantitative results could be ascertained. It appears at the present



time that the high exchange current which causes the nonpolarizability of the Al(III)/Al(O) electrode may well be due to an unknown intermediate species.



CONCLUSION

This thesis attempted to show the existence of  $\text{Al}_2\text{Cl}_7^-$  in the melt system used and to explain the destabilization of the higher valence states of metal ions in terms of the great covalent strength of the terminal Al-Cl bond. It was further argued that the overall charge on a metal ion can also be lowered by the reaction with neutral metal atoms thus giving rise to cluster formation.

Several problems, however, which are common to all molten salt system remain. The ions  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  can be shown to exist by various methods. Conductance measurements show that these anions, together with the cations, are the current carriers. But if an electrolysis is done the species reacting at the electrodes are  $\text{Al(III)}$  and  $\text{Cl}^-$ , according to the  $\text{Al(III)}/\text{Al(O)}$  and  $\text{Cl}_2/\text{Cl}^-$  couples which can also be realized. It is especially this problem which makes the evaluation of the processes at the  $\text{Al(III)}/\text{Al(O)}$  electrode conceptually difficult.

No precise ideas can be formed as to the type of the cluster ions. If they fill the empty spaces between the large  $\text{Al}_2\text{Cl}_7^-$  anions the question arises as to whether their complexity is defined by the available space or not. This space in itself may not be constant should further polymerization of the  $\text{Al}_2\text{Cl}_7^-$  species occur.

Although several points concerning the ternary  $\text{AlCl}_3^-$



NaCl-KCl have been clarified it is felt that much more work needs to be done before a complete understanding of this system is obtained.



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